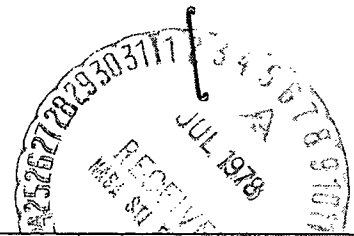SPACE THERMAL CONTROL
DEVELOPMENT

FINAL REPORT

December 1971

Contract NAS8-25183

Lockheed

HUNTSVILLE RESEARCH & ENGINEERING CENTER

LOCKHEED MISSILES & SPACE COMPANY

A GROUP DIVISION OF LOCKHEED AIRCRAFT CORPORATION

HUNTSVILLE, ALABAMA

LOCKHEED MISSILES & SPACE COMPANY, INC.

HUNTSVILLE RESEARCH & ENGINEERING CENTER

HUNTSVILLE RESEARCH PARK

4800 BRADFORD DRIVE, HUNTSVILLE, ALABAMA

SPACE THERMAL CONTROL
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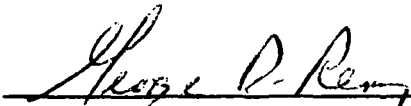Contract NAS8-25183

Prepared for National Aeronautics and Space Administration
Marshall Space Flight Center, Alabama 35812

by

M. J. Hoover
P. G. Grodzka
M. J. O'Neill

APPROVED: _____

George D. Reny, Manager
Aeromechanics Dept.

_____

J. S. Farrior
Resident Director

FOREWORD

This report presents the results of experimental studies performed on various phase change materials (PCMs). The work reported essentially fulfills the contract requirements set forth in Task II in Modification 1 to the original contract. Task I involved completion of a PCM handbook which was completed in September 1971. The handbook has been published as a NASA Contractor Report 61363 dated September 1971. Work accomplished on the contract prior to Modification 1 appears in the Lockheed report LMSC-HREC D162884. Task II in modification 1 is comprised of the following specific items:

> Supply detailed experimental information on the performance of various PCM candidates. Important thermal and physical properties are to be defined, using methods and apparatus developed in this study and previous studies. Experimental information will be obtained on the performance of various PCM/Filler combinations. Specific considerations will include ways to improve the thermal diffusivity of PCM systems, the effects of thermal cycling, and the selection of additional candidate materials.

This experimental research and development program is sponsored by the George C. Marshall Space Flight Center, National Aeronautics and Space Administration, Huntsville, Alabama. Miss Barbara E. Richard is the Contracting Officer's Representative. Dr. P. G. Grodzka, Research Specialist in the Aeromechanics Department of Lockheed's Huntsville Research & Engineering Center, is the principal investigator.

SUMMARY

The results of experimental investigations on a number of various Phase Change Materials (PCMs) and PCMs in combination with metals and other materials are reported. The experiments conducted were designed to yield information pertinent to spacecraft thermal control usage among various PCM and PCM/filler combinations. The evaluations include the following PCM system performance characteristics: PCM and PCM/Filler thermal diffusivities, the effects of long-term thermal cycling, PCM-container compatibility, and catalyst effectiveness and stability. Also reported are the results of additional conceptual and literature studies to identify new PCMs in various temperature ranges, to improve PCM performance, and to identify new PCM applications.

On the basis of the simple tests that were run in the present study, it is concluded that three PCMs designated in a previous study as prime PCMs demonstrated performance acceptable enough to be considered for use in prototype aluminum thermal control devices. These three PCMs are lithium nitrate trihydrate with zinc hydroxy nitrate catalyst, acetamide, and myristic acid. Of the fillers tested, aluminum honeycomb filler was found to offer the most increase in system thermal diffusivity.

CONTENTS

LIST OF ILLUSTRATIONS

NOMENCLATURE

A	area
C_p	specific heat at constant pressure
E	energy
h	cell height
k	thermal conductivity
m	mass
PCM	phase change material
R	thermal resistance
T	temperature
t	thickness
x	distance coordinate

Greek

α	thermal diffusivity
β	heating rate
ΔH_f	latent heat of fusion per unit mass
$\Delta \theta$	change in time
ρ	mass density
θ	time

Subscripts

comp	component being thermally protected by PCM system
container	PCM container

F	filler material
fin	metallic fin within PCM package
max	maximum
melt	at the PCM melting point
mounting plate	plate to which component is mounted (cold plate)
package	PCM thermal control package
PCM	phase change material
PCM package	PCM thermal control package
SL	at the solid-liquid interface
T	total

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CONCLUSIONS AND RECOMMENDATIONS

On the basis of the tests that were run in the present study, it is concluded that three PCMs designated in a previous study as prime PCMs demonstrated performance acceptable enough to be considered for use in prototype aluminum thermal control devices. These three PCMs are lithium nitrate trihydrate with zinc hydroxy nitrate catalyst, acetamide, and myristic acid. Of the fillers tested, aluminum honeycomb filler was found to offer the most increase in system thermal diffusivity.

The studies conducted have served to help define experimental concepts by which the PCM potential of large numbers of different classes of materials for a number of varied applications can be easily and rapidly tested. Undoubtedly numerous materials will be discovered which promise potential as PCMs. To test each one in full-scale prototype devices is obviously inefficient. On the basis of the experimental evaluations conducted in the present study the following procedure is recommended for evaluating a potential PCM for a given application:

1. A DSC thermogram on the potential PCM as received is taken.

2. A sample of the potential PCM is placed in an "inert" test container and another sample placed in an identical test container along with a piece of material, usually aluminum or other metal, which will contain the PCM in the hardware device.

3. The two test containers are heated and cooled through 50 cycles.

4. DSC thermograms are taken on samples of the cycled PCM and the aluminum pieces and containers examined for signs of attack.

5. The thermal diffusivity of the potential PCM is determined by the method developed in the present study or by some other suitable technique.

The information generated in following the outlined procedure (or approximate modification thereof) should provide sufficient information on which to base a first judgement of the PCM potential for a given application of a candidate material.

The studies conducted with regard to increasing PCM thermal diffusivity indicate a need for parametric analytical studies of various PCM/Filler ratios and geometries. At present no theoretical guides exist for optimizing PCM/Filler ratios and geometries. Some simple parametric studies, therefore, would provide practical guidance in this respect. Such studies would also provide insight and incentive for exploring theoretical relationships between system thermal diffusivity and PCM/Filler ratios and geometries.

Section 1
INTRODUCTION

The science and technology of phase change material (PCM) thermal control appears to be attracting a widening interest. Thermal control based on melting and freezing processes is currently being used or under consideration for a large range of space applications. The principle of PCM thermal control is briefly described as follows: A PCM is a material which undergoes a phase change, such as a change from a solid to a liquid, with a large accompanying absorption of latent heat and without a large elevation in temperature. The reverse process of freezing is accompanied by the liberation of the heat fusion as the PCM changes from a liquid to a solid, also without any appreciable elevation in temperature.

By the processes of melting and freezing, the PCM offers a reversible system which can act as either a heat sink or heat source, as required, at essentially constant temperature. The latent heat of fusion which can be either absorbed or liberated is many times greater than the specific heat. In the case of water, for example, the latent heat is 80 times greater than the specific heat. Theoretically, the advantages of PCM thermal control are many. Such a passive system requires no moving parts and it can operate reversibly for indefinite lengths of time. The desired temperature for control can be selected from a wide variety of PCM candidates.

The characteristics of an ideal PCM have been defined. In general, an ideal PCM would have the following features:

- High Heat of Fusion: This property defines the available energy and may be considered on a weight basis or a volume basis.

- Reversible Solid-to-Liquid Transition: The composition of the solid and liquid phases should be the same with no super-cooling or heating on freezing or melting.

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- High Thermal Conductivity and Diffusivity
- High Specific Heat and Density
- Long Term Reliability During Repeated Cycling
- Dependable Freezing Behavior
- Low Volume Change During Phase Transition
- Low Vapor Pressure
- Nontoxic and Noncorrosive

Actual material behavior will deviate from the ideal to varying extents because no one material has all of the desirable properties to the degree that would be ideal. A PCM is expected to provide isothermal control for a specified time in a particular application, so tradeoffs exist in selecting the most ideal PCM for a particular application. The present work is concerned with defining and generating the basic data needed to evaluate PCM performance. Judgments on PCM performance cannot be based solely upon the property data available from literature. A melting point of $291^{\circ}K$ is reported for glycerol, for example. However, glycerol is almost impossible to freeze, even when it is stored in liquid nitrogen. Many other materials also supercool without the formation of a true solid phase. Other materials decompose readily when they are heated, and some solid materials sublime without melting. The effects of cycling through alternate melting and freezing cycles, as well as compatibility with container materials used for packaging PCM systems, must for the most part be studied experimentally. Experimental studies conducted on PCMs in the present study were designed to evaluate performance characteristics pertinent to spacecraft thermal control and include PCM and PCM/Filler thermal diffusivities, the effects of long-term thermal cycling, PCM-container compatibility, and catalyst effectiveness and stability.

Section 2
EXPERIMENTAL STUDIES OF THERMAL DIFFUSIVITY

2.1 ROLE OF THERMAL DIFFUSIVITY IN PCM PERFORMANCE

Thermal diffusivity is defined by the relationship $\alpha = k/\rho C_p$ where α is the thermal diffusivity, k is the thermal conductivity, ρ the density, and C_p the specific heat. Thermal diffusivity may be represented as a time rate of temperature movement through a material. A large value indicates the ability of the material to equalize temperature differences within itself.

The thermal diffusivities of most nonmetallic materials are about 10^3 orders of magnitude lower than that of the metals. The thermal conductivities are also extremely low, comparable to the best insulators. Paraffin PCMs for example, are better insulators than rock wool. The temperature of melted paraffin may rise to the boiling point with solid paraffin adjacent to the boiling paraffin. In such cases, undesirable temperature gradients develop which seriously interfere with PCM system performance.

An important area of PCM technology is concerned with increasing the thermal diffusivity of non-metallic PCMs so that extreme temperature excursions can be avoided. In order to assess various ways of increasing thermal diffusivity, it was necessary to develop a method for determining thermal diffusivities of pure and filled PCMs. The preliminary development of the method used in the present study is reported in Ref. 1. Complete details and further refinements are presented in Appendix A of this report. In the present study, the thermal diffusivities of a number of PCMs and PCM/Filler combinations were determined by this method with precisions ranging from approximately 5 to 50%.

2.2 EXPERIMENTAL EVALUATION OF PCMS AND PCM/FILLER COMBINATIONS

The obvious way to improve the thermal diffusivity of a nonmetallic PCM is to pack it into an open structure of metal. Therefore, thermal diffusivities were evaluated for pure PCMs and PCM/Filler combinations in order to assess the difference. Thermal diffusivities for pure PCMs are presented in Table 2-1, and thermal diffusivities for PCM/Filler combinations are presented in Table 2-2. The data indicate that aluminum honeycomb offers the most improvement in thermal diffusivity compared to the others tested. However, other types of fillers conceivably could offer at least as much improvement. Aluminum fins are currently being used by some investigators in preference to honeycomb because of the problems encountered with obtaining good contact between honeycomb and the cold plate (Ref. 2). Heat pipes as fillers also could offer system improvement since they have nearly infinite thermal conductivity. Reference is made to Section 8, page 8-1 which discusses concepts for improving system performance. Detailed information on filler optimization can be found in Ref. 3 which includes:

- Amount of filler required for a particular application.
- Effects of bond and contact thermal resistance between filler and cold plate.
- Three-dimensional heat transfer effects within the filler.

The tests with the honeycomb as a filler left some doubt as to what was actually measured. When honeycomb touches both plates of a PCM container, it can act as a shunt for heat transfer. Therefore a series of tests was made in which water was used as a PCM and in which the honeycomb was placed so that it did not touch both plates. The first test was made with aluminum honeycomb in contact with the upper plate which is the heated plate, as shown in Table 2-3. The second test was made with the honeycomb in the middle of the cell, touching neither plate.

Table 2-1

THERMAL DIFFUSIVITIES FOR PCMS

PCM System	Thermal Diffusivity $cm^2/sec \times 10^{-3}$
Water	1.48 1.20 avg. 1.34 ± 0.14 (reported value of 1.35)[*]
Myristic Acid Solid	2.44 1.87 1.84 avg. 2.05 ± 0.26
Liquid	1.33
Acetamide Solid	38.2
Lithium Nitrate Trihydrate (liquid)	1.80

[*]James, D.W., "The Thermal Diffusivity of Ice and Water Between -40 and +60°C," J. Materials Sci., Vol. 3, (1968), pp. 540-543.
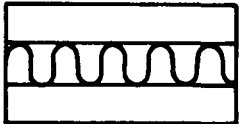
Table 2-2

MEASURED VALUES OF THERMAL DIFFUSIVITY
OF VARIOUS PCM-FILLER SYSTEMS*

PCM System	Thermal Diffusivity $cm^2/sec \times 10^3$
$LiNO_3 \cdot 3H_2O$ with no filler	1.8 1.8 avg. $\overline{1.8} \pm 0.0$
$LiNO_3 \cdot 3H_2O$ + Aluminum powder + surface-active agent 8/1 PCM/Filler Ratio	1.6 0.6 avg. $\overline{1.1} \pm 0.5$
$LiNO_3 \cdot 3H_2O$ + Aluminum gauze 8/1 PCM/Filler Ratio	3.0 2.0 avg. $\overline{2.5} \pm 0.5$
$LiNO_3 \cdot 3H_2O$ + Aluminum honeycomb 8/1 PCM/Filler Ratio	3.2 4.2 avg. $\overline{3.7} \pm 0.5$
$LiNO_3$ $3H_2O$ + Alumina (Al_2O_3) foam 8/1 PCM/Filler Ratio	3.2 1.9 avg. $\overline{2.6} \pm 0.6$
$LiNO_3$ $3H_2O$ + Alumina (Al_2O_2) powder 8/1 PCM/Filler Ratio	1.9 2.8 avg. $\overline{2.4} \pm 0.5$

*Data presented in this table are less precise than those presented in Tables 2-1 and 2-3 because data reduction procedures in the two cases differ. See Appendix A, page A-1 for details.

Table 2-3

THERMAL DIFFUSIVITY OF VARIOUS WATER/
HONEYCOMB COMBINATIONS

Honeycomb Configuration	Thermal Diffusivity $cm^2/sec \times 10^{-3}$
— Top — Bottom	6.6 6.9 avg. $\overline{6.8} \pm 0.2$
— Top — Bottom	6.6 6.5 avg. $\overline{6.6} \pm 0.1$
— Top — Bottom	1.4 1.3 avg. $\overline{1.4} \pm 0.1$

The results show that thermal shunting did not occur to any appreciable extent with the honeycomb and test cells used, and that the presence of honeycomb did indeed improve considerably the thermal diffusivity of the PCM/honeycomb system.

Section 3
EXPERIMENTAL STUDIES OF LONG TERM CYCLING EFFECTS

3.1 POSSIBLE EFFECTS OF THERMAL CYCLING

Since PCMs are required to operate reversibly by freezing and melting as heat is removed or added, it is important to know what effects thermal cycling has on PCMs. Each thermal cycle might effect a degree of PCM decomposition. The net result might, therefore, be a progressive deterioration of PCM performance. The compatibility of PCM and container metal, usually aluminum, might also be dependent on cycling since changes in compatibility can occur with changes in temperature. A PCM could be compatible with aluminum at room temperature and then become corrosive when elevated to the melting point. Catalyst stability and effectiveness are still other performance parameters which may be affected by thermal cycling. A catalyst might become ineffective because of progressive dissolution or chemical reaction. Cycling could also affect the distribution of impurities normally present in a PCM and thus alter PCM performance. In view of the possible effects that can occur during melting and freezing, cycling tests were conducted on several PCM candidates.

3.2 EXPERIMENTAL METHOD

The present study was concerned primarily with acquiring performance data on specific PCMs; i.e., the four PCM prime candidates lithium nitrate trihydrate, myristic acid, methyl fumarate, and acetamide. Another aim, however, was to develop an experimental evaluation method which would be simple, general, and informative enough for large numbers of different kinds of PCMs. As a result, two test methods were employed to evaluate the effects of long term thermal cycling on PCM stability and performance. The first test involved subjecting the four prime PCM candidates, myristic acid, methyl

3-1

fumarate, acetamide, and lithium nitrate trihydrate, to 50 cycles of melting and freezing. The PCMs were then examined visually to determine the effects of the cycling. In the second method, the heat absorbed or liberated as the PCM candidate, oxazoline wax TS970, was heated and cooled at preset rates, was tracked by means of a differential scanning calorimeter (DSC). The DSC yields a thermogram on the substance being heated or cooled as shown in Fig. 3-1. The peaks occur during melting or freezing of the substance, and the
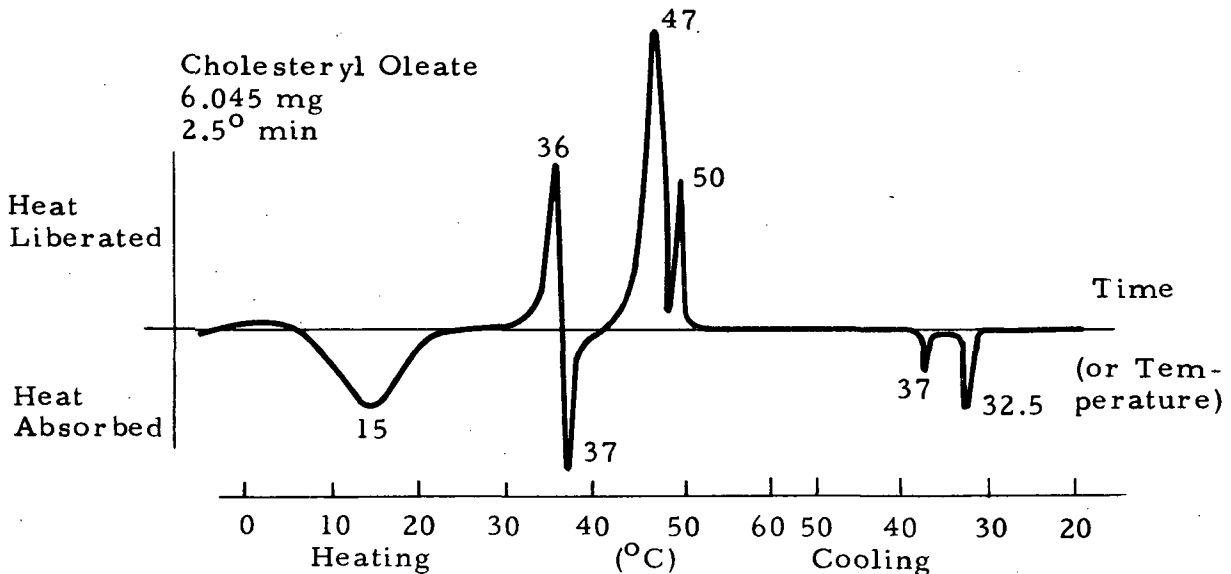
Fig. 3-1 - Thermal Profile of Cholesteryl Oleate

areas under the peaks give quantitative data on the amounts of heat liberated and absorbed. Appendix B, page B-1 describes the principle of the DSC in more detail.

In the first test method, the PCMs tested were contained both in aluminum canisters and in glass test tubes. Aluminum is most often used for PCM containers. The aluminum canisters used for some of the tests are ordinarily used to contain photographic film. The tops of the canisters contain iron and a rubber seal. Glass test tubes were also used in some tests. Small pieces of aluminum were placed with the PCM in the glass tubes. A programmed timing device was installed to turn a heater on and off automatically at preset intervals. The temperature was cycled in such a manner that the PCMs were

3-2

elevated to a temperature sufficiently above their melting points to melt all of the PCMs and cooled to temperatures low enough to ensure freezing. Cycling was continued through 50 melting-freezing cycles. Cycling was then discontinued to examine the PCMs. PCM stability and compatibility with container were evaluated by visual inspection after the cycling.

3.3 RESULTS OF CYCLING

The results of the thermal cycling tests employing the first described method are presented in Table 3-1.

Table 3-1

OBSERVATIONS ON PCMS IN ALUMINUM AND GLASS
CONTAINERS AFTER 50 THERMAL CYCLES

PCM	Test Containers	
	Aluminum Container	Glass Container plus Aluminum Chips
Methyl Fumarate	Aluminum Discolored	Aluminum Discolored
Lithium Nitrate Trihydrate	No Degradation	Evidence of Sublimation. No Degradation
Acetamide	No Degradation	No Degradation. Evidence of Sublimation
Myristic Acid	No Degradation	No Degradation

The results indicate that methyl fumarate (or an impurity therein) is seriously corrosive to aluminum. The evidence of sublimation shown by methyl fumarate and acetamide should be kept in mind because special arrangements will be required to fill containers with any sizable amounts of these two materials; i.e., molten PCM will evolve copious smoke of sublimate. In closed containers, however, the sublimation should present no adverse effects.

In the series of tests employing the DSC, cycling was investigated in depth with PCM Oxazoline Wax TS970. Heating rates of 1.2, 2.5, 5, 10 and 20 degrees Kelvin per minute were applied consecutively to melt the PCM. In all cases, the PCM melting points were the same, and no signs of degradation were observed. The procedure was repeated to give a total of 10 melting cycles. The thermal profiles for all cycles were essentially identical.

The DSC was also used to investigate the effect of cycling on freezing behavior. High purity indium, benzoic acid, and Oxazoline Wax TS970 were melted at the same rate (10°K per minute) and cooled at different rates. Indium, used as a standard or reference, supercooled 4°K at five different cooling rates — 1.2, 2.5, 5, 10 and 20°K per minute. PCM benzoic acid with a purity of 99.992% consistency supercooled 44°K with the same cooling rates. Oxazoline Wax TS970 supercooled 20°K at two cooling rates of 5 and 10°K per minute.

The rates of cooling selected did not have any significant effects with the three materials tested. However, with cooling rates other than the ones available and other materials, complete consistency should not necessarily be expected. Furthermore, the large amount of supercooling exhibited by high purity benzoic acid (44°K) further demonstrates that high purity, expensive PCMs do not necessarily exhibit ideal behavior.

Section 4

PERFORMANCE PROFILES ON FOUR PRIME PCM CANDIDATES

The data presented in Sections 2 and 3 on the four prime PCM candidates lithium nitrate tryhydrate, myristic acid, methyl fumarate, and acetamide, along with other pertinent experimental observations, are summarized here by individual PCM material. Technical grade materials were used for all testing.

4.1 LITHIUM NITRATE TRIHYDRATE

Correct preparation of this salt hydrate is of extreme importance. The best way to prepare lithium nitrate trihydrate consists of adding a slight excess of the anhydrous salt ($LiNO_3$) over the calculated amount to water, and warming the solution to a temperature a few degrees above $293^{\circ}K$, the melting point of the trihydrate. The trihydrate solution is then filtered and contained as quickly as possible in a stoppered bottle.

The preparation and properties of the nucleating catalyst, zinc hydroxy nitrate are given in Appendix C, page C-1.

Zinc hydroxy nitrate has successfully nucleated lithium nitrate trihydrate through repeated melting-freezing cycles as demonstrated in the Solar Home Heating experiment, Section 6, page 6-1. Samples of PCM and catalyst from this experiment are still showing good freezing behavior.

The nucleating catalyst is insoluble in the PCM. It should, therefore, be placed directly in the test or final container and it should not be placed in the PCM which is then poured into the test container. The latter course may result in PCM-catalyst separation.

Lithium nitrate is extremely responsive to the water content of air, absorbing or liberating water depending on the humidity. The freezing

4-1

behavior of this PCM is greatly affected by the presence of water. Therefore, exposure to air should be kept at a minimum.

The maximum amount of water vapor absorbed from air by lithium nitrate trihydrate was 45% by weight. After this amount of water was gained from standing open to the air, the sample began to lose weight.

The thermal diffusivity of lithium nitrate trihydrate was determined:

$$\alpha = 1.9 \times 10^{-3} \text{ cm}^2/\text{sec}$$

In cycling tests, lithium nitrate trihydrate performed well through alternate melting/freezing cycles, provided the temperature did not go higher than 364°K. The catalyst is stable up to this temperature. After 50 alternate freezing/melting cycles, the PCM and its catalyst did not show any visible evidence of attack on aluminum.

4.2 MYRISTIC ACID

Myristic acid was tested for thermal diffusivity, and the values obtained are:

Solid: 2.1×10^{-3} cm^2/sec
Liquid: 1.3×10^{-3} cm^2/sec

Myristic acid melts with no observable sublimation. It is nontoxic and easy to work with. After 50 freezing/melting cycles, it showed no attack on aluminum, steel and rubber. No unusual behavioral characteristics have been observed.

4.3 METHYL FUMARATE

Methyl fumarate sublimes profusely when it is heated. One sample completely sublimed away before it could be melted. In closed containers, however, no unusual vapor pressures or other problems were exhibited.

4-2

After thermal cycling in a glass container, methyl fumarate exhibited good freezing/melting behavior with no sign of degradation after 50 cycles. Methyl fumarate was not compatible with aluminum, rubber or steel. The incompatibility with aluminum may be due to the methyl fumarate or to its impurities.

4.4 ACETAMIDE

Since one investigator reported that acetamide decomposes strongly near its melting point (Ref. 4) acetamide was investigated for behavior characteristics. Previous literature searches and experimental evaluation performed at Lockheed-Huntsville led to the selection of acetamide as a prime candidate (Ref. 5).

Tests have shown that acetamide sublimes profusely near its melting point. No evidence of decomposition has been observed. Several references state that acetamide can be purified by distillation (Ref. 6). Since its boiling point is 494.3°K, it would indicate stability to at least this temperature.

Acetamide was cycled through 50 alternate melting/freezing cycles with no apparent ill effects. Although it sublimes on heating, no vapor pressure problems were encountered in the cycling tests (reported vapor pressure: 1 mm at 338°K).

For a nonmetallic compound, acetamide has an unusually high thermal diffusivity, 33×10^{-3} cm^2/sec (Ref. 1) for the solid. The thermal diffusivity of water is 1.35×10^{-3} cm^2/sec, and most other nonmetallic PCMs have thermal diffusivities close to that of water or lower.

Acetamide was tested for compatibility during the 50 melting/freezing cycles. It is compatible with aluminum. Steel and rubber however, are not compatible with acetamide.

4-3

Section 5

PCM SYSTEM ANALYSES

During this contract period, thermodynamic and heat transfer analyses of one-dimensional PCM thermal control systems were conducted. These analyses and their results are reported in detail in Ref. 3. A brief review of the theory and results of the analyses is presented in this report for completeness, but Ref. 3 should be consulted for a more detailed treatment.

5.1 ONE-DIMENSIONAL PCM SYSTEM MODEL AND ASSUMPTIONS

To demonstrate the thermodynamic and heat transfer principles which apply to PCM systems in general, the simple PCM package in Fig. 5-1 will be considered. For simplicity, the following assumptions will be made for this example:

1. The components are one-duty cycle electronic components, like those found on launch and reentry vehicles;

2. Power generation of constant magnitude $(\dot{Q})$ begins at $\theta = 0$ and ceases at $\theta = \Delta\theta$;

3. Heat transfer is purely one-dimensional conduction;

4. At $\theta = 0$, the PCM is solid and the entire package is at T_{melt};

5. Sensible heat storage is small compared to latent heat storage, so that a nearly linear temperature distribution occurs during the melt process, as shown in Fig. 5-2.

6. Power generation ceases at $\theta = \Delta\theta$ just as the PCM becomes completely melted; and

7. No contact resistances, convection, or three-dimensional effects will be considered.

5.2 CONSERVATION RELATIONS FOR THE SYSTEM

For the system under consideration, several relations can be derived.

5-1

A-A

Components

Section A-A

Mounting
Plate

t_{PCM}

package

A-A

PCM ———— Fins ———— Container
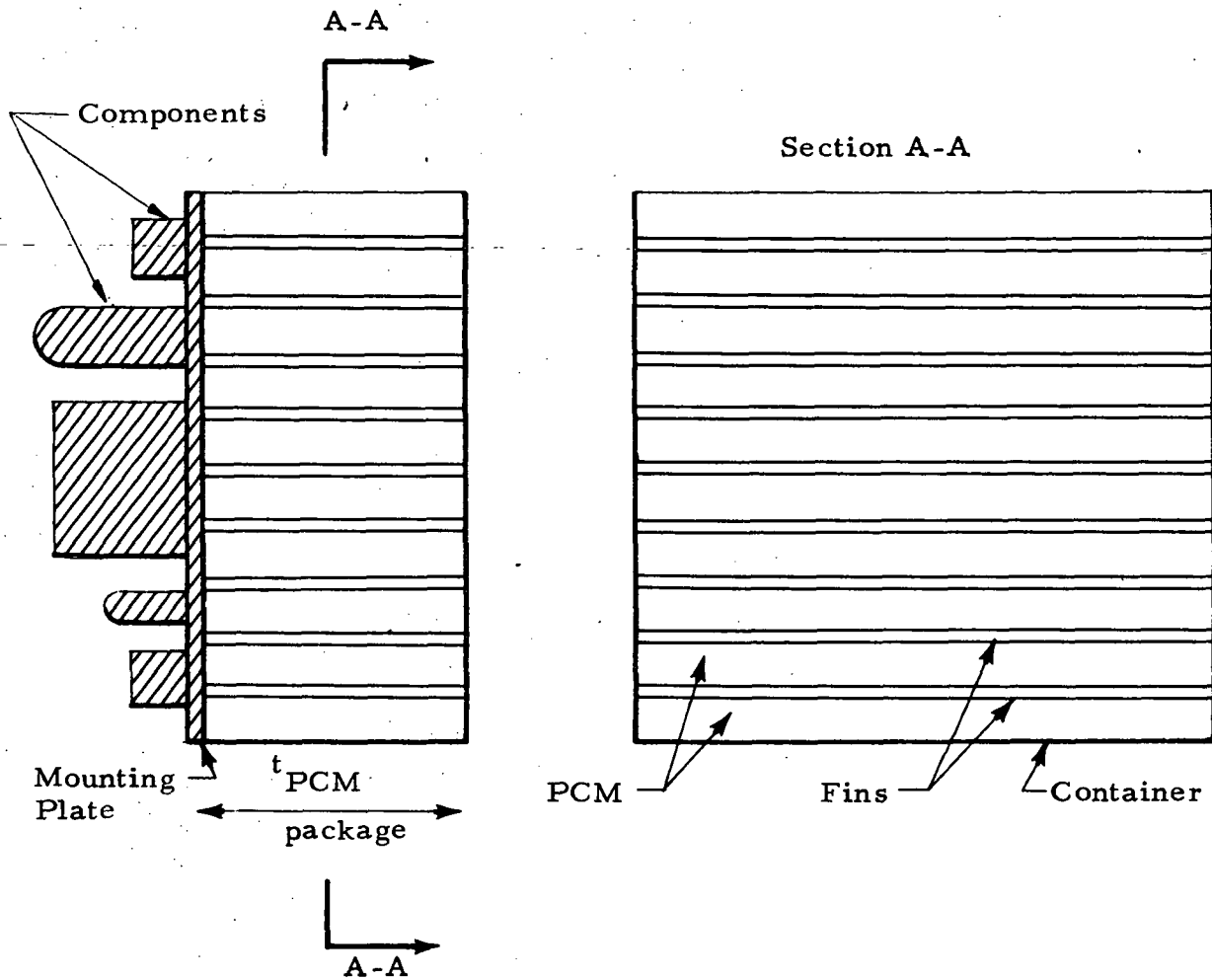
NOTE: Total Cross-Sectional Area = $A_{mounting\ plate}$

PCM Cross-Sectional Area = A_{PCM}

Filler Cross-Sectional Area = A_F

Fig. 5-1 - One-Dimensional PCM System

5-2
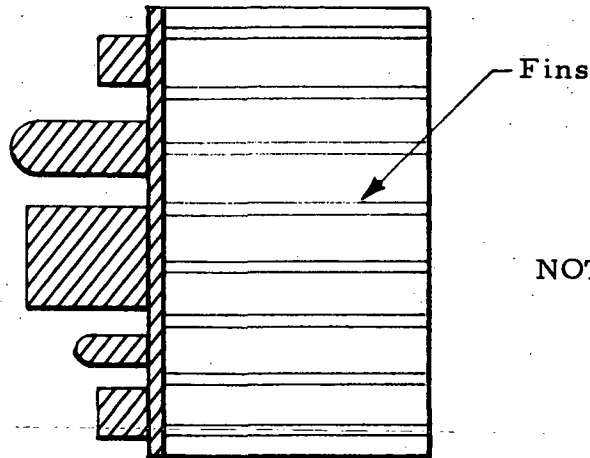
NOTE: x_{SL} is the location of the solid-liquid interface.

$\theta = 0$ (Power On)

$\theta = 1/4 \, \Delta\theta$

$\theta = 1/2 \, \Delta\theta$

$\theta = 3/4 \, \Delta\theta$

$\theta = \Delta\theta$ (Power Off)
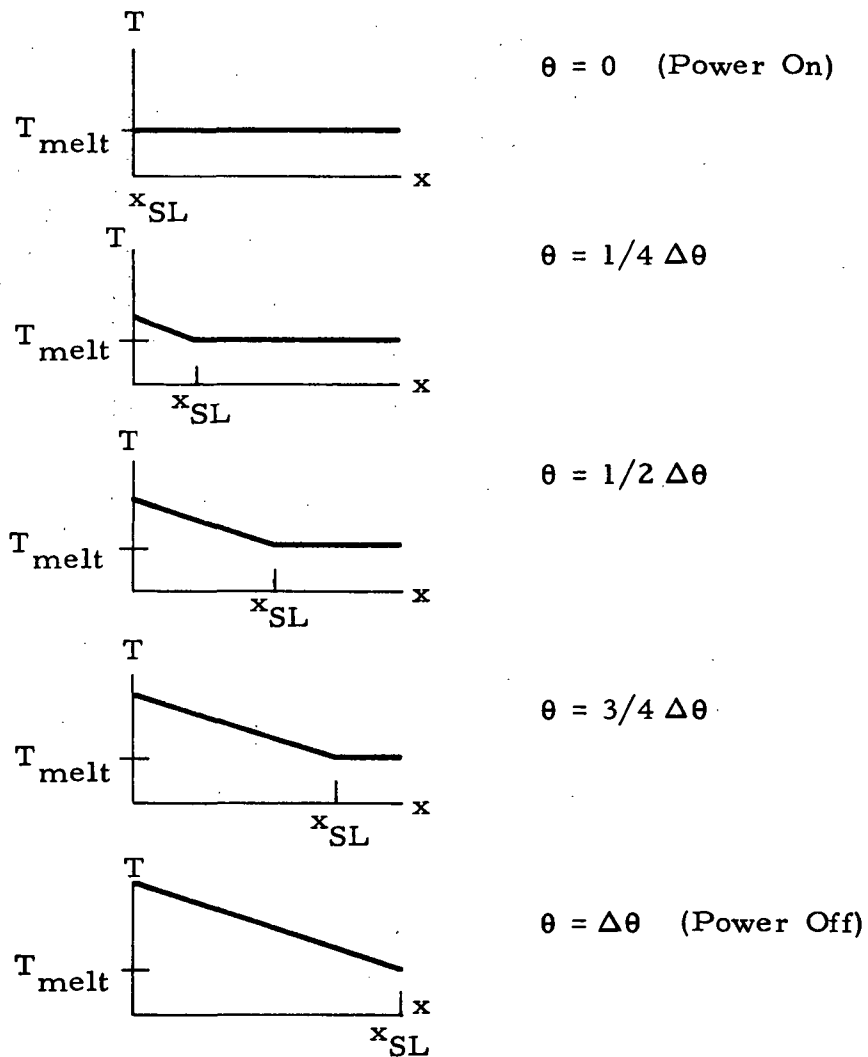
Fig. 5-2 - Temperature Distribution Within PCM Package

5-3

These relations are given below:

Conservation of Energy Relation:

(Datum: $E = 0$ when filler and PCM are at T_{melt} throughout and PCM is solid throughout)

$$\dot{Q}\Delta\theta = E_{max} = \rho_{PCM} A_{PCM} t_{PCM\,package} \Delta H_f$$

$$+ \left[\rho_F A_F C_{p_F} + \rho_{PCM} A_{PCM} C_{p_{PCM}} \right] \frac{1}{2} (T_{max} - T_{melt}) \left(t_{PCM\,package} \right) \quad (1)$$

Maximum Temperature Relation:

$$T_{max} = T_{melt} + \frac{\dot{Q}\, t_{PCM\,package}}{k_T A_{mounting\,plate}} \quad (2)$$

Total Conductance Relation:

$$k_T A_{mounting\,plate} = k_{PCM} A_{PCM} + k_F A_F \quad (3)$$

Total Cross-Sectional Area Relation:

$$A_{PCM} + A_F = A_{mounting\,plate} \quad (4)$$

Conservation of Mass Relation:

$$m_T = (\rho_{PCM} A_{PCM} + \rho_F A_F)\, t_{PCM\,package}$$

$$+ \rho_{container}\, t_{container} \left[2 A_{mounting\,plate} + 4\, t_{PCM\,package} \sqrt{A_{mounting\,plate}} \right] \quad (5)$$

5-4

5.3 PCM COMPUTER PROGRAM DEVELOPMENT

If the following variables are known:

(1) $\dot{Q}$,

(2) $\Delta\theta$,

(3) ρ_{PCM},

(4) ΔH_f,

(5) ρ_F,

(6) C_{p_F},

(7) $C_{p_{PCM}}$,

(8) T_{melt},

(9) $A_{mounting\ plate}$,

(10) k_{PCM},

(11) k_F,

(12) $\rho_{container}$,

(13) $t_{container}$,

the following unknowns will be left in the five equations:

(1') A_{PCM}

(2') $t_{PCM\ package}$

(3') A_F,

(4') T_{max},

(5') k_T,

(6') m_T.

With five equations and six unknowns, one of the unknowns can be taken as a parameter and the other five unknowns can then be determined as functions of that parameter. If A_F is chosen as the parameter, or equivalently $A_F / A_{mounting\ plate}$ is chosen as a dimensionless parameter, then the other five unknowns can be determined in terms of $A_F / A_{mounting\ plate}$. A computer program

was coded under this contract to solve the set of equations parametrically in $A_F/A_{\text{mounting plate}}$.

Note that the variables (1) through (13) are known for particular applications, as shown below:

(A) Variables (1) and (2) are fixed by the component's operating requirements;

(B) Variables (3), (4), (7), (8) and (10) are fixed by the choice of PCM;

(C) Variables (5), (6) and (11) are fixed by the choice of filler material;

(D) Variable (9) is fixed by available space limitations and component geometry;

(E) Variables (12) and (13) are fixed by choice of container material and by structural requirements.

The usefulness of the parametric data obtainable with the computer program is described in the following section.

5.4 OPTIMIZED PCM SYSTEM DESIGN

Assume that an optimum PCM thermal control system is to be designed for the components shown in Fig. 5-1. Suppose further that the components generate $\dot{Q} = 1000$ watts for a period $\Delta\theta = 1$ hour. Let space limitations dictate a mounting plate area of 0.093 square meters and let aluminum be the container and filler material. Also let structural requirements dictate a container thickness of 0.254 cm. Suppose the best PCM available for the temperature range of interest has a melt temperature of 300°K, and its thermal properties are:

$$\rho_{PCM} = 1.602 \text{ gm/cm}^3$$

$$k_{PCM} = 0.519 \text{ W/m-}^\circ\text{K}$$

$$c_{p_{PCM}} = 1.6736 \text{ J/gm-}^\circ\text{K}$$

$$\Delta H_f = 232.4 \text{ J/gm.}$$

Inputting these given requirements into the computer program yields the parametric data shown in Fig. 5-3. These data show the total package mass, the total package thickness, and the maximum temperature the components will achieve as functions of filler amount. Now suppose the components cannot operate correctly if their temperature exceeds $350^\circ K$. From the curve for T_{max} in Fig. 5-3, it is obvious that for $A_F/A_{mounting\ plate}$ less than 10%, the T_{max} will exceed $350^\circ K$. Therefore, filler must be added to the package such that $A_F/A_{mounting\ plate}$ exceeds 10%. Inspection of the mass and thickness curves in Fig. 5-3 shows a monotonic increase of each of these variables with increasing $A_F/A_{mounting\ plate}$. Therefore, if $A_F/A_{mounting\ plate}$ is greater than 10%, the package weight and thickness will be greater than their corresponding values at $A_F/A_{mounting\ plate}$ = 10%. Therefore, the optimum quantity of filler is 10%.

Therefore, for the given requirements of this PCM problem, the optimum PCM thermal control system would have the following design:

$$A_F/A_{mounting\ plate} = 10\%$$

$$Mass = 17\ kg$$

$$Thickness = 10\ cm.$$

To summarize, for a given one-dimensional PCM thermal control problem with variables (1) through (13) known, the optimum design can be obtained from the parametric output data of the computer solution of Eqs. (1) through (5). For a listing and further explanation of the computer program consult Ref. 3.
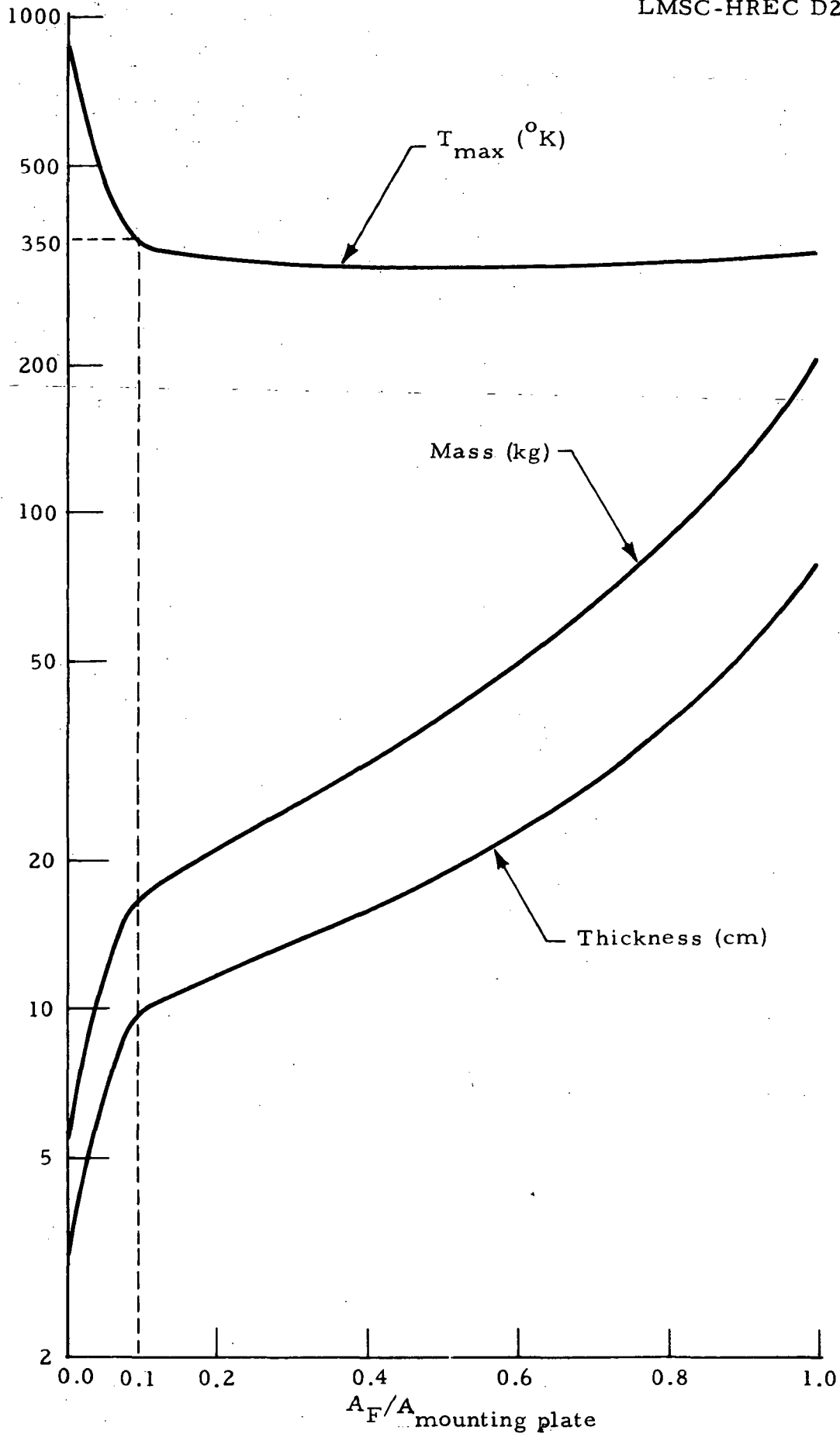
Fig. 5-3 - Parametric PCM Computer Program Data

Section 6

NEW APPLICATIONS FOR PCMS

6.1 SOLAR ENERGY AND PCM

In the course of the present studies, it became evident that some of the PCM materials being studied appeared to have great potential for solar home heating and cooling. Therefore, a small project was conducted to obtain an estimate of the feasibility of PCM home heating and cooling, using solar energy (Ref. 7).

In order to assess the merits of PCM home heating and cooling, two miniature test houses were constructed and instrumented. The houses are made of styrofoam and are 15-3/4 by 13-1/4 by 9-3/4 inches in dimensions. One house contains PCM material and the other house is used as a reference. Forty holes were cut into the roof of each house. Small aluminum canisters ordinarily used as containers for photographic film were filled with a promising PCM (lithium nitrate trihydrate plus a catalyst). These canisters were inserted into the roof holes. The roof containing the canisters filled with PCM was then covered with aluminum foil (Fig. 6-1). The canisters for the reference house were filled with water. All conditions were kept the same except for the material in the canisters. A hydrothermograph, an instrument that records temperature, was placed in each house. Both houses were placed outside where they were exposed to the Alabama summer climate for a number of weeks.

Typical temperature recordings obtained in the two houses are shown below. In every case, the temperature of the model house was cooler than the temperature of the reference house during the hot part of the day. Also, the temperature during the cold hours at night was not as low as that of the reference house. Further studies to improve design and to determine optimum operating parameters will undoubtedly increase system efficiency.

6-1

SOLAR ENERGY

ROOF

LAYER OF FOIL,
REFLECTING
SIDE DOWN

INSULATED
STYROFOAM
WALL

CONTAINERS
WITH PCM
MATERIAL

RECORDING
THERMOMETER
UNIT

METALLIC THERMOMETER

ROTATING DRUM
WITH GRAPH PAPER
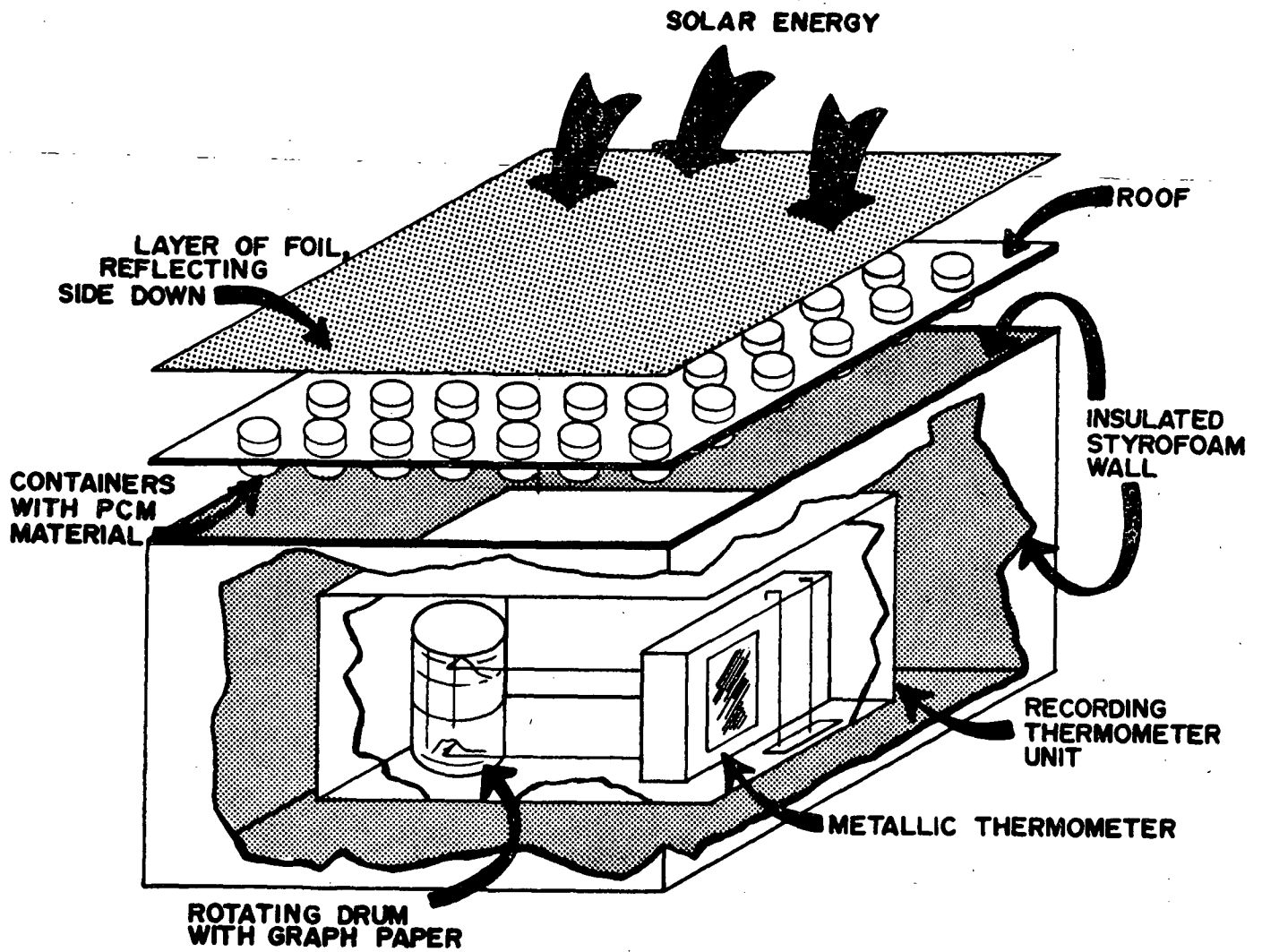
Fig. 6-1 - PCM-Solar Energy House

6-2

DAILY RECORD, 21-22 JUNE

	High ($^{\circ}$F)	Low ($^{\circ}$F)	Fluctuation ($^{\circ}$F)
Reference House	98	63	35
Model House	87	68	19

Daily High Temperatures ($^{\circ}$F)			Daily Low Temperatures ($^{\circ}$F)		
Reference House	Model House	Degrees Cooled	Reference House	Model House	Degrees Heated
94	86	- 8	66	69	+3
99	89	-10	69	71	+2
103	94	- 9	71	72	+1
91	84	- 7	65	70	+5
97	87	-10	65	68	+3

6.2   HEAT PIPES AND PCM

The extremely high values of thermal conductivity exhibited by heat pipes naturally brings up the question of the advantages of heat pipe/PCM systems. A heat pipe can possibly offer advantages in several ways:

- PCM system performance may be improved by the use of many small heat pipes as fillers to improve PCM/system thermal diffusivity.
- PCM can absorb heat delivered by a heat pipe and store it by melting.
- Stored heat acquired during melting can be returned by the PCM for possible usage.

The advantages offered by a heat pipe in conjunction with PCM were investigated in two tests. The first test made use of PCM as a heat sink in conjunction with a heat pipe to deliver heat from a heat source. The heat delivered by the heat pipe to the PCM was absorbed by the PCM at a temperature no higher than the melting point of the PCM. In the second test, PCM was used as a heat

6-3

source instead of a heat sink. A description of the method and results of the PCM-heat pipe experiments is given as follows.

6.2.1 PCM as a Heat Sink

Lithium nitrate trihydrate was used as a PCM heat sink in the apparatus shown in Fig. 6-2. A second test used an equal weight of water as a heat sink so that a comparison could be made with the PCM heat sink. Test conditions for both tests were identical except for the material used as a heat sink, PCM or water.

The heat source (A) consists of 100 millimeters of heated water placed in an insulated calorimeter flask. A heat pipe is placed with one end in the heat source and the other end in the heat sink (B). The quantity of heat transmitted to the heat sink is determined from (1) the drop in temperature of a known weight of water in the heat source and (2) from a cooling curve of the heat source without a heat storage material.

The following results were obtained:

1. The same amounts of heat are transported by the heat pipe to the heat sink in a given time in both tests.

2. The rate of heat transport to the heat sink is, therefore, the same for water and for PCM.

3. PCM absorbs heat at constant temperature when its melting point is reached. The change in temperature of the heat sink containing PCM was therefore only $4^{\circ}K$ (Fig. 6-3).

4. Water in the heat sink shows, on the other hand, a $35^{\circ}K$ increase in temperature (Fig. 6-3).

5. At the conclusion of the tests, the temperature of PCM in the heat sink remains constant, while that of the water starts to decrease.

From these results it is concluded that PCMs will offer the following advantages as a heat sink material for heat pipes:

● A PCM can act as an efficient "cold heat sink" because it can absorb large quantities of heat at a low temperature.
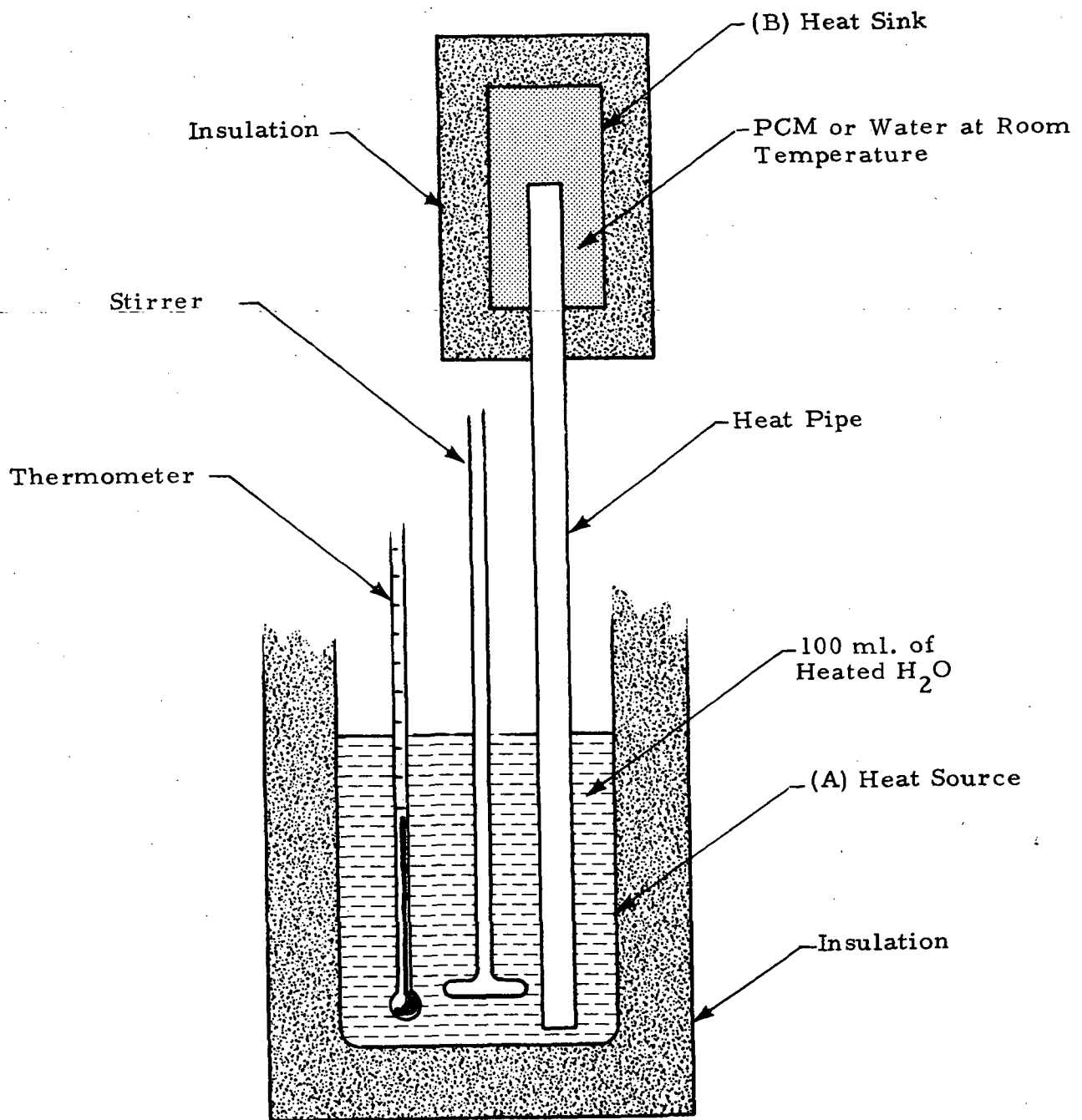
Fig. 6-2 - PCM with Heat Pipe
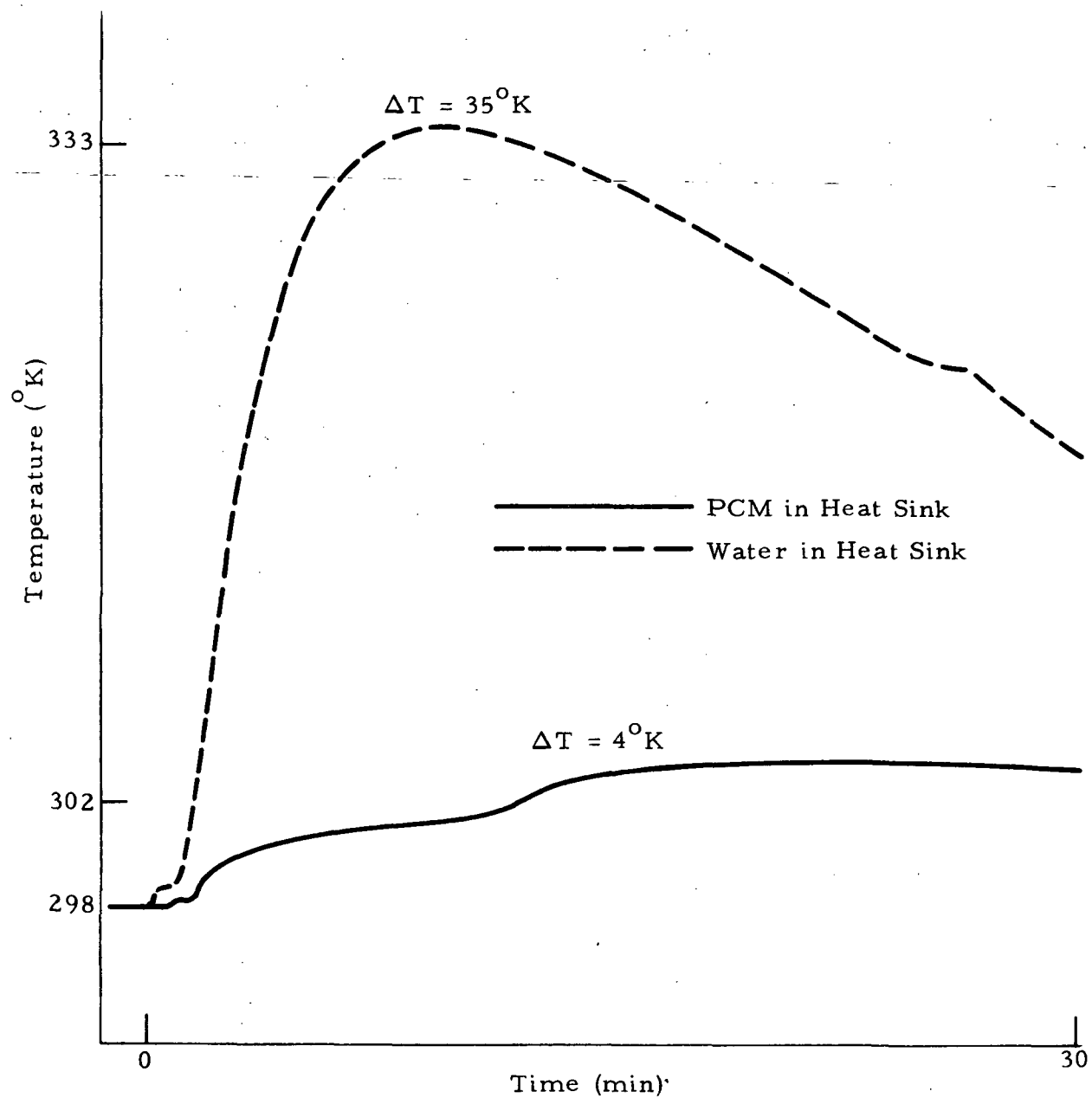
Fig. 6-3 - Heat Sink Temperature vs Time

- The latent heat of fusion offered by a PCM is from 50 to 80 times larger than the heat capacity of heat transfer materials.

- The relatively large amount of heat absorbed by the PCM heat sink is in essence stored and, therefore, can be regenerated for subsequent use.

6.2.2 PCM as a Heat Source

An experiment was devised to determine if the heat of fusion liberated by a freezing PCM is effective as a heat source in conjunction with a heat pipe. The heat pipe used for tests contains methanol (boiling point = $338^{\circ}K$). Therefore, a PCM was selected which has a melting point above the boiling point of methanol in the heat pipe. Benzoic acid with a melting point of $394.8^{\circ}K$ was selected to test as a PCM heat source.

The experimental setup is the same as that pictured in Fig. 6-3, except that the heat source (A) consists of melted PCM and the heat sink (B) is a measured amount of water at room temperature.

The PCM was heated and melted so that the latent heat of fusion would be available as the heat source. One end of the heat pipe was placed in the melted PCM at $394.8^{\circ}K$ and the other end was placed in a heat sink of water at $297.4^{\circ}K$. The PCM began to freeze and within minutes, the water in the heat sink showed a temperature rise of $18^{\circ}K$.

For comparison, a heat source of silicone oil at $394.8^{\circ}K$ was tested in the same apparatus. All test conditions were identical except for the material used as a heat source. The water in the heat sink showed a temperature rise of $3.3^{\circ}K$ (Fig. 6-4).

Results of both tests showed that a calculated 255 calories were transferred to the heat sink of water by the PCM. The silicone oil delivered 63 calories to the heat sink. From these tests, it appears that the heat of fusion liberated by a freezing PCM is much more effective as a heat source than the heat capacity of a heat transfer material, as predicted from calculations.

6-7
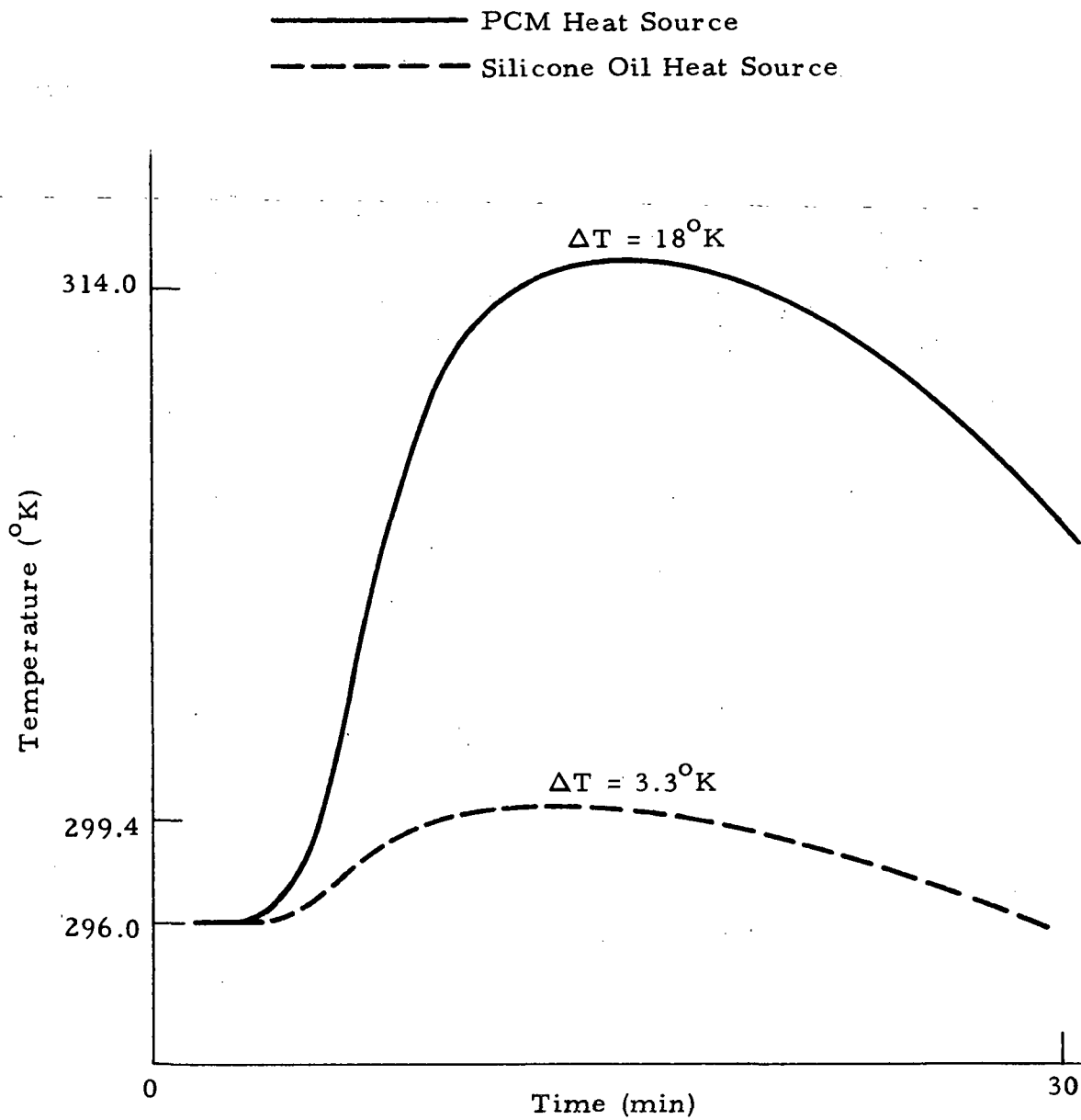
Fig. 6-4 - Heat Sink Temperature vs Time with PCM Heat Source

6.3   PCM THERMAL CONTROL FOR CRYSTAL GROWING

Since PCM techniques offer an essentially isothermal environment, an experiment was devised for growing crystals in a PCM thermally controlled environment. Crystals grown from a solvent need a constant temperature for good growth because the solubility of a solid in a solvent varies with temperature. An insulated container with PCM was used to grow both seed crystals and large crystals. Visual inspection showed that crystals grown in the PCM container had better optical qualities, such as clarity and refractivity, than crystals grown outside the PCM container. Crystal faces and angles were sharply defined in several cases. From these preliminary tests, it appears that PCM techniques offer a good thermal control method for crystal growing.

Section 7
POTENTIAL NEW PCMS

The demand for PCMs having low melting points has prompted a search for materials with fairly low melting points. Therefore, a number of low melting potential PCMs were identified from various sources. No attempt has been made to fit these materials into a particular application. Materials suitable for one application may be undesirable for others. A high latent heat of fusion is desirable in a PCM since it defines the available energy. However, when other properties are more critical, materials having moderate values of heats of fusion may be attractive. For this reason, the Freons are included. High heats of fusion are not expected with members of this series, but they may be attractive for some applications because they are nonflammable and have low toxicity.

General information about normal and associated liquids is given in Appendix D, page D-1. The properties of a PCM in the liquid state are generally dependent upon whether the liquid PCM is a normal or associated liquid. A series of new bismuth alloys and gallium alloys is presented which increases the number of possible metallic PCMs. Gases and gas hydrates are presented as potential low-melting PCMs.

7.1 METALLIC PCMS

7.1.1 Alloys of Gallium

Data were found for the specific composition of six gallium alloys. The heat of fusion of most gallium alloys is around 42 joules per gram. The composition and melting points of these alloys are given on page 7-2 (Ref. 8).

Composition (% by Weight)	Melting Point	
	(°K)	(°C)
Ga (21.5% In) (16% Sn)	283.9	10.7
Ga + 24% In	288.9	15.7
Ga + 12% Sn + 6% Zn	290	17
Ga + 8% Sn	293	20
Ga + 5% Zn	298	25
Ga + ~1% Aℓ	299.5	26.3

7.1.2 Alloys of Bismuth

The following list of low-melting bismuth alloys was supplied by Metal Specialities, 35 Drouve Street, Bridgeport, Connecticut, 06604.

PARTIAL LIST AND COMPOSITIONS
LOW MELTING POINT ALLOYS OF BISMUTH

Melting Point or Range (°K)	Composition				
	Bi	Pb	Sn	Cd	In
320	44.7	22.6	8.3	5.3	19.1
320 - 325	44.7	22.6	11.3	5.3	16.1
330 - 333	49.1	17.9	11.6	0.5	20.9
	47.5	25.4	12.6	9.5	5.0
334	32.5		16.5		51.0
334 - 338	48.0	25.6	12.8	9.6	4.0
343 - 346	50.5	27.8	12.4	9.3	
343 - 347	50.0	25.0	12.5	12.5	
344	38.4	30.8	15.4	15.4	
344 - 361	42.5	37.7	11.3	8.5	
347 - 367	50.0	39.0	4.0	7.0	
350 - 355	50.0	39.0	3.0	8.0	
352	57.0		17.0		26.0
354 - 358	50.3	39.2	1.0	8.0	1.5
356 - 365	52.0	31.7	15.3	1.0	
360 - 362	51.1	39.8		8.1	1.0
361 - 367	51.4	31.4	15.2		2.0
364 - 367	52.0	31.7	15.3		1.0
365	51.6	40.2		8.2	
368 - 377	56.0	22.0	22.0		
368 - 388	50.0	25.0	25.0		
371 378	52.2	37.8	10.0		
371	51.6	41.4	7.0		
373	50.0	32.2	17.8		
375 - 381	54.5	39.5	6.0		
376 - 390	53.0	42.5	4.5		

7.2 PATENTED PCMS

7.2.1 Zer-O-Ice

Zer-O-Ice is a semi-solid paste, probably consisting of water with a thickener and combination of inhibitors to prolong shelf life. A puncture in the container probably serves the purpose of accommodating volume changes during melting-and-freezing. The melted material does not leak out of the container due to its gelatinous consistency. The material may be repeatedly frozen and melted, as recommended by the supplier. Property data supplied by the distributer are as follows:

pH:	9.5 to 10.2
Melting Point:	$273^{o}K$
Heat of Fusion:	approximately 335 joules per gram (80 calories per gram)
Cost:	$2.40 per dozen pints; $3.27 per dozen quarts (hermetically sealed rectangular packages)
Supplier:	R.M. Hollingshead Corporation, Camden, N.J.

7.2.2 Transit-Heet

A series of PCM materials with thirty-nine different melting points ranging from 222 to $505^{o}K$. Some of the series may be suitable for reversible melting and freezing and others may be suitable for one-time operation only. The heat of fusion of the series is 123 to 371 joules per gram. Densities range from 0.97 to 2.60 grams per cubic centimeter. Property data supplied by the distributor on the 39 transit-heets are presented in Table 7-1, as supplied by the manufacturer.

Supplier:	Royal Industries 2040 East Dyer Road Santa Ana, California, 92705

Table 7-1

APPLICATION DATA FOR TRANSIT-HEET[*]

Trans. Temp.	Density (lb/ft³) (least)	Heat of Fusion		Specific Heat (Btu/lb)		Suitable for Application as			Efficiency	
		Btu/lb	Btu/ft³	Solid	Liquid	General Use	Special Design	Exp. Only	Weight	Space
(-) 60	81	53	4,300	0.4	0.7		X		L	L
(-) 28	79	82	6,000	0.4	0.7		X		L	L
(-) 6	68	118	8,200	0.4	0.75	X			L	M
(-) 2	67	92	6,100	0.4	0.68	X			L	L
(-) 1	77	103	8,000	0.4	0.7	X			M	M
1	73	126	9,200	0.4	0.7	X			H	H
3	61	134	8,200	0.45	0.8	X			H	M
12	64	115	7,300	0.45	0.8	X			M	L
24	71	127	8,900	0.4	0.7	X			H	M
24A	64	115	7,300	0.45	0.82	X			M	L
27	63	142	8,800	0.45	0.82	X			VH	M
28	57	142	8,500	0.5	0.85	X			VH	M
40	100	75	7,500	0.31	0.60	X			L	L
52	88	70	6,200	0.32	0.60	X			L	L
60	98	95	9,300	0.40	0.60		X		L	H
65	94	80	7,500	0.42	0.78	X			L	L
75	94	100	9,400	0.4	0.7			X	M	H
77	91	125	11,400	0.43	0.70			X	H	VH
85	100	73	7,300	0.4	0.7			X	L	L
86	90	132	11,900	0.45	0.73		X		H	VH
89	91	108	9,800	0.42	0.79	X			M	H
95	90	120	10,800	0.5	0.6			X	H	VH
97	95	114	11,000	0.37	0.65		X		M	VH
108	113	60	6,800	——	——			X	L	L
116	81	160	13,000	0.41	0.80			X	VH	VH
120	100	90	9,000	——	——			X	L	H
130	125	72	9,200	0.5	0.7			X	L	H
136	81	114	9,200	0.47	0.77		X		M	H
140	120	90	10,800	0.5	0.7			X	L	VH
147	100	113	11,300	——	——			X	M	VH
150	135	82	11,000	0.45	0.70		X		L	VH
160	100	100	10,000	——	——			X	M	H
170	135	131	18,000	0.28	0.70			X	H	VH
180	92	70	6,500	——	——			X	L	L
188	91	70	6,400	0.48	0.70		X		L	L
190	103	112	11,500	0.36	0.80		X		M	VH
240	94	74	6,800	0.4	0.7			X	L	L
450	106	159	16,800	0.33	0.39			X	VH	VH
350-450	168	128	21,500	0.2	0.2			X	H	VH
CO₂ -109°F	96 (solid)	241	23,100	0.23	0.20	X			VH	VH
H₂O	62.4	144	8,380	0.5	1.0	X			VH	M

[*]Data are presented as supplied by the Manufacturer.

Conversion Factors:

$$^\circ K = \frac{5}{9}\left[^\circ F + 459.67\right]$$

$$\text{Joules/kg-}^\circ K = \text{Btu/lb-}^\circ F\left[4.184 \times 10^3\right]$$

7.3 FREONS

The Freon series is a group of polyhalogenated derivatives of methane and ethane. They are non-flammable, have low toxicity, high vapor pressure, and have a high degree of chemical and thermal stability (Ref. 8). Stability results directly from the presence of fluorine atoms in the molecule. Generally, the more fluorine, the greater the stability. Freons contain fluorine, and in most cases, chlorine or bromine. Freons are used as refrigerants and as propellents in aerosol products because of low toxicity and lack of odor. Recently they have come into use as fire extinguishers. Freons are normal liquids and would be expected to give predictable and reliable performance as PCMs. However, the heats of fusion of normal liquids are low compared with associated liquids, probably half as large or less (see Appendix D, page D-1. When other properties such as low toxicity, nonflammability, and reliable behavior are more important than a high heat of fusion, they may be useful for certain applications.

Freon-11

Synonyms:	Trichlorofluoromethane, Fluorotrichloromethane
Description:	Colorless liquid
Formula:	$F\,C\,C\ell_3$
Melting Point:	$162^\circ K$ $(-111^\circ C)$
Boiling Point:	$297.2^\circ K$ $(24.1^\circ C)$
Density:	1.494 grams/cm^3 at $290.3^\circ K$ $(17.2^\circ C)$
(Ref. 9)	

Freon-12

Synonym:	Dichlorodifluoromethane
Description:	Colorless, odorless gas
Formula:	$C\,C\ell_2\,F_2$
Melting Point	$115^\circ K$ $(-158^\circ C)$
Boiling Point	$224^\circ K$ $(-29^\circ C)$
Vapor Pressure:	5 atm at $217^\circ K$ $(16^\circ C)$
(Ref. 9)	

7-5

Freon-21

Synonym:	Dichlorofluoromethane
Description:	Heavy, colorless gas
Melting Point:	$138^{\circ}K$ ($-135^{\circ}C$)
Boiling Point:	$282^{\circ}K$ ($8.9^{\circ}C$)
Density:	1.48 grams/cm^3
Vapor Pressure:	2 atm at $301.3^{\circ}K$

(Ref. 9)

Freon-22

Synonym:	Chlorodifluoromethane
Description:	Gas
Melting Point:	$127^{\circ}K$ ($-146^{\circ}C$)
Boiling Point:	$232.4^{\circ}K$ ($-40.8^{\circ}C$)
Density:	Same as that of air at $273^{\circ}K$ ($0^{\circ}C$)

(Ref. 9)

Carbon Tetrafluoride

Synonyms:	Tetrafluoromethane, fluorocarbon 14
Description:	Colorless gas
Formula:	CF_4
Melting Point:	$89^{\circ}K$ ($-184^{\circ}C$)
Boiling Point:	$145^{\circ}K$ ($-128^{\circ}C$)
Density of Liquid:	1.96 grams/cm^3 at $89^{\circ}K$ ($-184^{\circ}C$)
Hazard:	Nonflammable. Moderately toxic by inhalation.

(Ref. 10)

7.4 WAXES AND OILS

This group is represented already by two PCMs, oxazoline waxes ES 254 and TS 970. The heat of fusion of the latter is 172 joules per gram (41 calories per gram) as determined by DSC. It is possible that the heats of fusion of

other waxes or oils may be similar. The amount of supercooling is given by
the difference in melting and freezing points. Data for PCM purposes is
lacking in the waxes and oils, as for most materials.

Wax or Oil	Melting Point ($^{\circ}$K)	Freezing Point ($^{\circ}$K)
Sugar Cane Wax	328 - 335	—
Carbowax 1540	313	—
Carbowax 4000	323 - 328	—
Coconut Oil	299 - 301	295
Olive Oil	277 - 300	267 - 275
Palm Oil	—	304 - 312
Poppy Seed Oil	255	255
Bayberry Wax	313 - 317	—
Candelilla Wax	333	—
Carnuba Wax	356 - 364	353 - 353
Ceresine Wax	347 - 353	—
Chinese (Cerotin) Wax	353 - 356	—
Japan (Vegetable) Wax	326	—
Ocuba Wax	312.6	—
Spermaceti Wax	317 - 321	—

(Ref. 10)

7.5 LOW MOLECULAR WEIGHT COMPOUNDS

This category includes gases, gas hydrates, and possible aluminum
chloride eutectics.

1. Gases

    a. Ammonia (NH_3)

        ΔH_f = 452 joules/gram

      Melting Point (Ref. 8):   195.41°K

      Boiling Point (Ref. 8):   239.73°K

Vapor Pressure (Ref. 8) ^{o}K

1426.8 mm	253
3221.0 mm	273
6428.5 mm	293

b. Carbon Dioxide (CO_2)

ΔH_f = 452 joules/gram

Density: Solid 1.54 grams/cm^3

Melting Point: 195°K

2. Gas Hydrates

a. $NH_3 \cdot H_2O$

Melting Point: 196°K

b. $NH_3 \cdot 2 H_2O$

ΔH_f = 130 joules/gram

Melting Point: 176°K

7.6   ORGANICS[*]

1. Methyl Amine

Formula: $C H_5 N$

Melting Point: 179.6^{o}K

Heat of Fusion: 197.6 joules/gram

2. Formic Acid

Formula: $C H_2 O_2$

Melting Point: 281.4^{o}K

Heat of Fusion: 276.54 joules/gram

Corrosive

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[*]Data from Ref. 11.

3. n-Decane

    Formula: $C_{10}H_{22}$

    Melting Point: $243.4^{\circ}K$

    Heat of Fusion: A paraffin; probably in the range
                            200 to 256 joules/gram

4. Thiophene

    Formula: S CH: CHCH: CH

    Melting Point: $235^{\circ}K$

    Heat of Fusion: —

    Boiling Point: $357^{\circ}K$

    Density: 1.0583^{20} grams/ml

5. Furfurol

    Formula: $C_4H_3O\,CHO$

    Melting Point: $236^{\circ}K$

    Heat of Fusion: —

    Boiling Point: $435^{\circ}K$

    Density: 1.1598^{20} grams/ml

6. Sorbitol Monohydrate

    Formula: $(CH_{20}H)_5\,CHOH \cdot IH_2O$

    Melting Point: $328^{\circ}K$

    Heat of Fusion: —

7. Butanol Dihydrate

    Formula: $C_4H_9OH\quad 2H_2O$

    Melting Point: $273.5^{\circ}K$

    Heat of Fusion: —

Salt Hydrates

    (Heats of fusion not available)

Formula	Density[*] (gm/cm^3)	Melting Point[*] $(^{\circ}K)$
$LiI \cdot 3H_2O$	3.48	346
$BaI_2 \cdot 6H_2O$	—	298.7
$BF_3 \cdot 2H_2O$	1.63	279
$A\ell Br_3 \cdot 15H_2O$	—	265.6
$Fe\,Br_3 \cdot 6H_2O$	—	300
$Fe(CO)_6$	liq. 1.457^{21}	252
$FeC\ell_3 \cdot 6H_2O$	—	310

7.7 COMPOSITE PCMS

A new type of PCM which appears to have potential is a composite PCM.
An effective composite PCM might consist of (1) a high conductivity PCM such
as a metallic PCM with a low heat of fusion combined with (2) a nonmetallic
PCM of low thermal conductivity with a high heat of fusion. Such a composite
PCM should out-perform either PCM by itself. Metallic PCMs generally have
low heats of fusion: 25 joules/gram to 91 joules/gram. Nonmetallic PCMs with
heats of fusion of 240 joules/gram are common. However, most nonmetallic
PCMs have extremely low thermal conductivities and diffusivities, about 10^3
order of magnitude lower than metallic PCMs. They are extremely slow in
dissipating heat and equalizing temperature. A heat pulse by a component
results in a temperature gradient because of heat transfer problems. For
this reason, nonmetallic PCMs lose effectiveness as heat sinks.

A metallic PCM of high thermal conductivity next to the component, in
combination with a nonmetallic PCM with a high latent heat of fusion, may offer
the combined advantages of both types of PCMs.

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[*]Ref. 11.

Section 8
CONCEPTS FOR IMPROVING PCM SYSTEM PERFORMANCE

A PCM thermal control system has the unique potential of absorbing and liberating large quantities of heat by the processes of melting and freezing. The PCM offers a reversible system which can act as a heat sink or heat source without an elevation of temperature. An essentially isothermal control is maintained during PCM melting and freezing. Ideally when a component is introduced, heat generated by the component (such as a transistor) will be transferred into the PCM. The PCM will absorb the heat isothermally by the process of melting. When heat is removed from the system, the PCM can liberate heat isothermally by freezing. However, in practical situations a temperature gradient is required to transfer heat from the component into the PCM. Furthermore, the PCM may not liberate heat by freezing when heat is removed because of supercooling. A look into the basic factors affecting PCM system performance and several ways to improve performance are discussed in the following sections.

8.1   ROLE OF NUCLEATION

For one-time applications, PCM may be used as a heat sink through melting and not be required to perform reversibly by freezing. However, when reversible temperature control through alternate melting and freezing is required, nucleation and subsequent crystal growth become important.

Nucleation is the formation of the first crystals in a liquid PCM which are capable of spontaneous growth into large crystals. These first crystals, called nuclei, may be formed from the liquid itself or on a foreign particle in the system which acts then as a nucleating catalyst. Nuclei are generated from the liquid PCM itself at a temperature lower than the melting point. Ideally, the melting point and freezing point should be the same for reversible, isothermal control. However, many liquid PCMs cool far below the solid-liquid equilibrium temperature without any formation of the solid phase. This

phenomenon is supercooling. System failure can result from supercooling because when heat is taken away, the PCM does not freeze and liberate latent heat of fusion. Because of the difficulty in self-nucleating a liquid PCM, a search for ways to improve nucleation characteristics was initiated. One of the obvious ways to improve nucleation performance is to add a catalyst. The identification of a suitable catalyst, however, is a fortuitous event which at present has little scientific rationale.

8.2   NUCLEATION WITH ULTRASONICS

Ultrasonic waves reportedly nucleate gallium, a metallic PCM, by cavitation or the formation of tiny bubbles which can act as nuclei for crystal growth (Ref. 12). In the present study, cavitation was not observed in gallium with the ultrasonic device available for tests, but was clearly evident in several other liquid PCMs. Ultrasonics, however, did not noticeably affect the nucleation performance of any of the PCMs tested. Several observations made when PCM lithium nitrate trihydrate and its nucleating catalyst were placed in an ultrasonic field are:

- The catalyst was reduced to extremely fine particles and dispersed throughout the PCM, and
- A large number of extremely small crystals were formed.

Without an ultrasonic field, a few large crystals are obtained with the catalyst remaining at the bottom of the container. Although ultrasonic waves did not successfully nucleate a PCM in these preliminary tests, a device with a selection of wave lengths could possibly cause nucleation.

Two other effects of ultrasonics which could have significance in nucleation are stirring and particle agglomeration. A frequently used way to reduce supercooling is to stir a liquid as vigorously as possible. Stirring tends to produce more possible patterns for disoriented particles of liquid, and thus increases the chance of forming the right pattern for crystallization. Ultrasonics does offer a way to stir a passive system, possibly more effectively than other ways.

Particle agglomeration is another effect produced by ultrasonics which could have significance in PCM technology. This technique has been used in industry to collect fumes, dust, sulfuric acid mist, carbon black and other substances. The lightweight particles follow the rapid motion of the sound waves, whereas heavy ones cannot. In either gases or liquids, agglomeration ultrasonically involves turning the frequency to the particle size existing in the media. Results similar to the agglomeration of particles in a gas may be obtained in a liquid. The effect seems due to (1) collision of particles, and (2) adherence (Ref. 13). The adherence may be due to electric charges, or removal of surface films. Possibly nuclei too small to grow may be agglomerated by ultrasonic waves, either by adherence or by clumping together in an aggregate which might act as a large particle.

The role of ultrasonics in nucleation is too new to evaluate at the present time as to its effectiveness or the mechanisms involved. The effects of high frequency waves on liquids are many and may find use in several fields. It is interesting to note that both agglomeration and the opposite process of dispersion may be brought about by ultrasonic waves. Another interesting effect which might be useful is structural relaxations in associated liquids (many PCMs are associated liquids). These relaxations take place when one part of the molecule moves from one position to another under the effect of sound-wave energy (Ref. 8). A definite structure like that which occurs in associated liquids and polymer liquids, is required.

8.3 LAYERED PCMs

Heat transfer problems are perhaps the greatest obstacles to be overcome in improving PCM system performance. Materials with large heats of fusion on a weight basis generally have low thermal conductivities and diffusivities. Therefore, for reasonable heat fluxes, a very steep temperature gradient is required to transfer heat from the component to the PCM. This steep temperature gradient results in a large temperature excursion of the component (Ref. 14). A new type of PCM which may prove to have great potential in system performance is a composite or layered PCM. This type of PCM is illustrated in Fig. 8-1. A horizontal layering system is
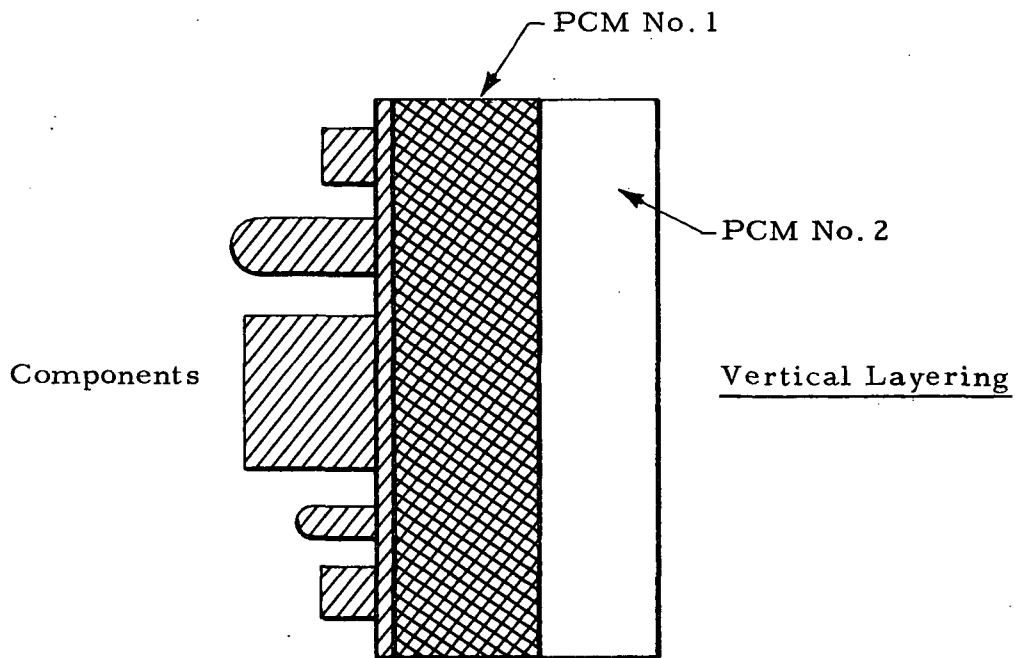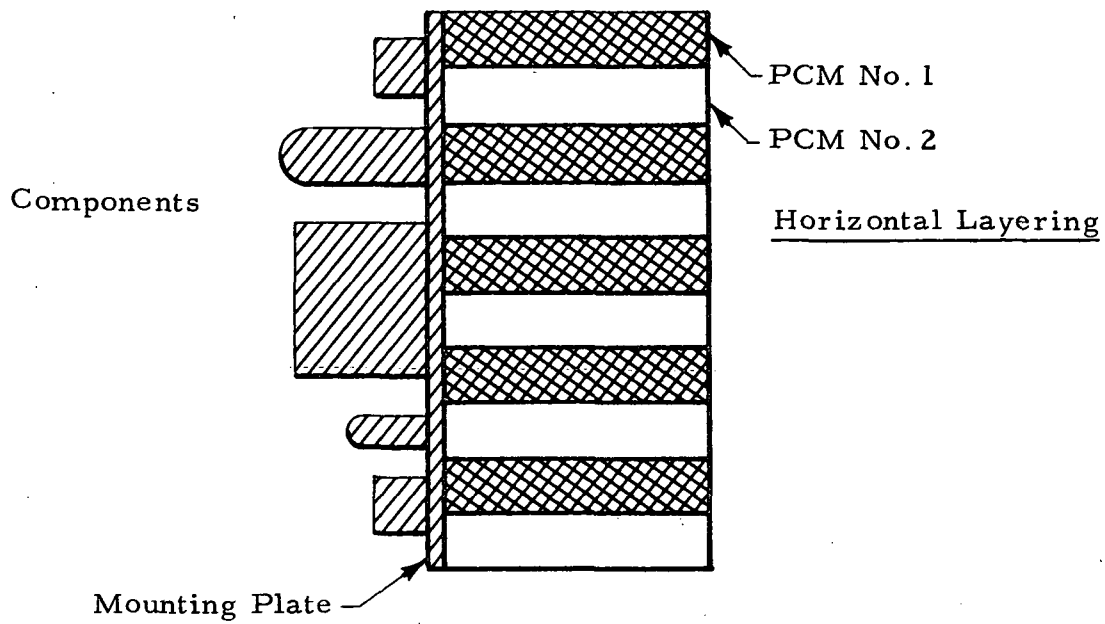
Fig. 8-1 - PCM System Improvement by Layering PCMs

depicted where PCM 1 represents a high thermal conductivity metallic PCM
with a relatively small heat of fusion. PCM 2 represents a relatively low
conductivity PCM with a relatively high heat of fusion. A practical example
might be gallium for PCM 1 and lithium nitrate trihydrate for PCM 2. For
certain heat transfer and energy storage requirements ($\dot{Q}$ and E_{max}), PCM 1
by itself might not meet the energy storage requirements without excessive
mass, and PCM 2 by itself might not meet the heat transfer requirements
without excessive temperature increase. However, used together, PCM 1
could serve to increase the effective thermal conductivity of the package,
while PCM 2 could serve as the large heat capacitance. The mutually bene-
ficial behavior of such a composite should therefore outperform either PCM
taken by itself.

The vertical layering technique also shown on Fig. 8-1 again pairs a
high conductivity, low heat of fusion PCM (No. 1) with a PCM of opposite
properties (No. 2). Similar to the horizontal layering example, a vertical
layering composite could conceivably outperform either PCM taken by itself
in certain thermal control applications. One immediate application for the
vertical composite is to use PCM 1 as a safety thermostat for the compo-
nent being protected. For example, during regular performance only PCM 2
would melt and freeze for thermal control, but a sudden power surge in the
component might try to push the component temperature above its maximum
allowable temperature. However, if PCM 1 melts below this maximum tem-
perature it will intercept the power surge heat and maintain the component
in its safe operating temperature range. Both layering configurations should
be analyzed to determine their benefits.

8.4   CONTACT RESISTANCE EFFECTS

Thermal contact resistances within PCM packages can seriously degrade
the performance of PCM thermal control systems. One example of this effect
can be seen in Fig. 8-2. The metallic fins within the package are attached to
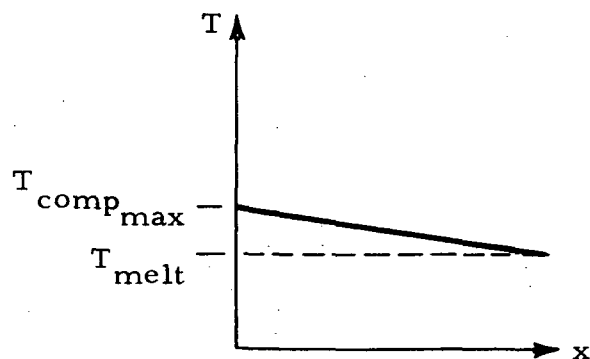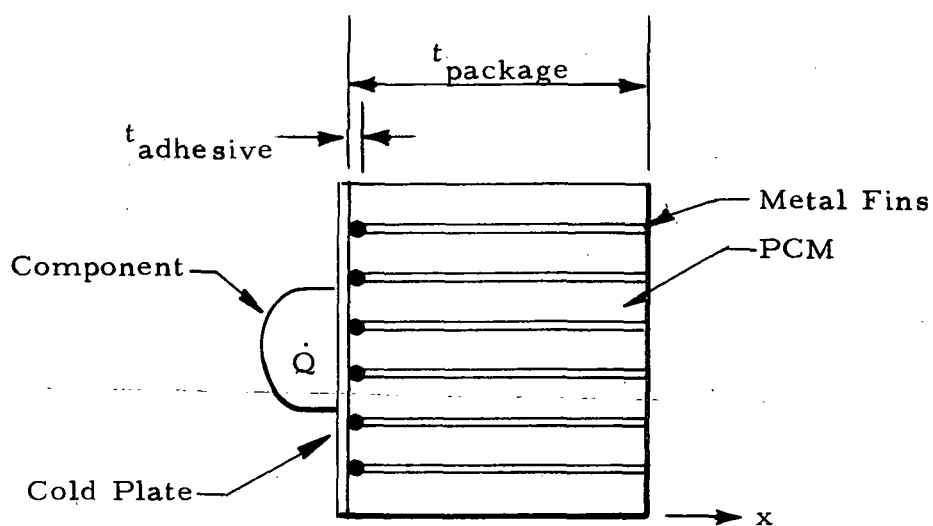
(a) Temperature Distribution at Total Melt Without
Adhesive Thermal Resistance
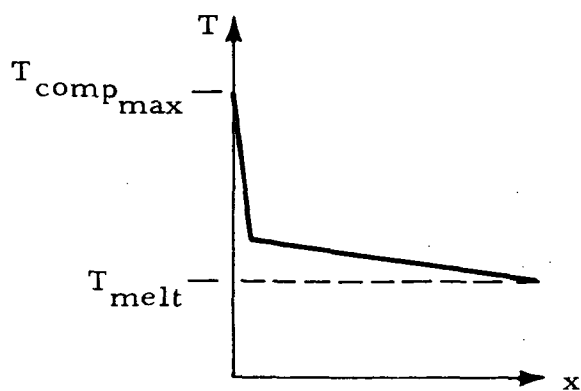
(b) Temperature Distribution at Total Melt With
Adhesive Thermal Resistance

Fig. 8-2 - The Effect of Adhesive Thermal Resistance on Component
Temperature Rise

the component mounting plate (cold plate) with a metal-filled adhesive. If the PCM in the package is initially in the totally frozen state and at the melt temperature throughout, and if a constant heat flux is then applied to the cold plate until all the PCM has melted, the temperature rise of the cold plate (and component) can be calculated. If this temperature rise is calculated with and without considering the thermal resistance of the adhesive bond, the net effect of the bond can be determined.

In terms of total package thermal resistance, the temperature rise of the component can be calculated as follows:

$$T_{comp_{max}} - T_{melt} = \dot{Q}\,(R_{tot})$$

If the adhesive thermal resistance is negligible and the PCM conductivity small,

$$R_{tot} = \frac{t_{package}}{K_{fin}\,A_{fin}}\,.$$

Therefore, the temperature rise of the component neglecting adhesive thermal resistance becomes:

$$\left(T_{comp_{max}} - T_{melt}\right)_{\substack{without \\ adhesive \\ resistance}} = \dot{Q}\left(\frac{t_{package}}{K_{fin}\,A_{fin}}\right)\,.$$

If, however, the adhesive resistance is not negligible, the total thermal resistance of the package becomes:

$$R_{tot} = \frac{t_{package}}{K_{fin}\,A_{fin}} + \frac{t_{adhesive}}{K_{adhesive}\,A_{fin}}\,,$$

(assuming $A_{adhesive} = A_{fin}$ and that $t_{package} >> t_{adhesive}$) .

8-7

Therefore, the temperature rise of the component with adhesive resistance becomes:

$$\left(T_{comp_{max}} - T_{melt}\right)_{\substack{with \\ adhesive \\ resistance}} = \frac{\dot{Q}}{A_{fin}} \left[\frac{t_{package}}{K_{fin}} + \frac{t_{adhesive}}{K_{adhesive}}\right] .$$

The ratio of temperature rise with adhesive resistance to the temperature rise without adhesive resistance will yield the magnitude of the degradation due to the adhesive resistance. Thus:

$$\frac{\left(T_{comp_{max}} - T_{melt}\right)_{\substack{with \\ adhesive \\ resistance}}}{\left(T_{comp_{max}} - T_{melt}\right)_{\substack{without \\ adhesive \\ resistance}}} = \frac{\frac{t_{package}}{K_{fin}} + \frac{t_{adhesive}}{K_{adhesive}}}{\frac{t_{package}}{K_{fin}}}$$

$$= 1 + \frac{t_{adhesive} \, K_{fin}}{t_{package} \, K_{adhesive}}$$

For a realistic application, the fin material is usually aluminum, and a recent Lockheed study[*] (Ref. 3) of metal-filled adhesive revealed that $K_{aluminum}/K_{adhesive}$ is equal to about 300. Thus, if a small PCM package is constructed with $t_{package}$ = 1 cm and a film of metal-filled adhesive is used to bond the fins to the cold plate such that $t_{adhesive}$ = 0.01 cm, the temperature rise ratio above can be numerically evaluated:

$$\frac{(Temperature\ Rise)_{\substack{with \\ adhesive \\ resistance}}}{(Temperature\ Rise)_{\substack{without \\ adhesive \\ resistance}}} = 1 + 300 \left(\frac{0.01}{1}\right) = 4 .$$

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[*] Bizzell, G. D., and M. P. Hollister, "Heat Pipes for Active Thermal Control of Spacecraft," Report for 1969 Independent Development Program, Dept. 62-63, LMSC/A965174, Lockheed Missiles & Space Company, Sunnyvale, Calif., 13 February 1970.

Therefore, it is apparent that the adhesive thermal resistance can cause the temperature rise of the component to quadruple the temperature rise without adhesive resistance. Since the usual purpose of such a PCM system is to minimize component temperature changes, the importance of the adhesive thermal resistance is evident. The designer of PCM systems should therefore give serious consideration to such resistances. The benefit of using metal-to-metal bonding via welding, soldering, etc., is also apparent from the above discussion.

The adhesive thermal resistance, the contact resistances between the adhesive and cold plate, between the adhesive and fin, and between the component and cold plate should be investigated by the designer of PCM thermal control systems.

Section 9

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Appendix A

METHOD FOR DETERMINING
THERMAL DIFFUSIVITY

Appendix A

A.1   EXPERIMENTAL APPARATUS

The basis of the method utilized in the present study depends upon maintaining a constant rate of temperature rise on one side of a test cell containing PCM (Fig. A-1). The thermal diffusivity (α) of a PCM is determined by:

- Applying a constant heating rate (β) to one place of the test cell containing PCM.

- Measuring the constant temperature difference (ΔT) between the heated and unheated plates of the test cell of height (h).

The equation relating these quantities is:

$$\alpha = \frac{\beta h^2}{2 \Delta T} \qquad\qquad (A.1)$$

A linear temperature programmer with a control thermocouple controls the heating rate. The linear temperature programmer used in the present study is part of a Fisher Differential Thermal Analyzer unit. The programmer varies the current to the infrared lamp according to the control thermocouple input. The heating rate of the copper plate at the upper end of the test cell is thus set at a constant value. Heating the test cell at the top is necessary to minimize convection currents.

A test cell can be made from a section of Plexiglass tubing with the open ends covered by aluminum foil. A small inlet drilled into the cell is convenient for filling the cell with PCM, and it also serves as an overflow (Fig. A-2). The PCM can be injected into the test cell with a hypodermic syringe. The test cell should be well insulated to minimize heat leakage.
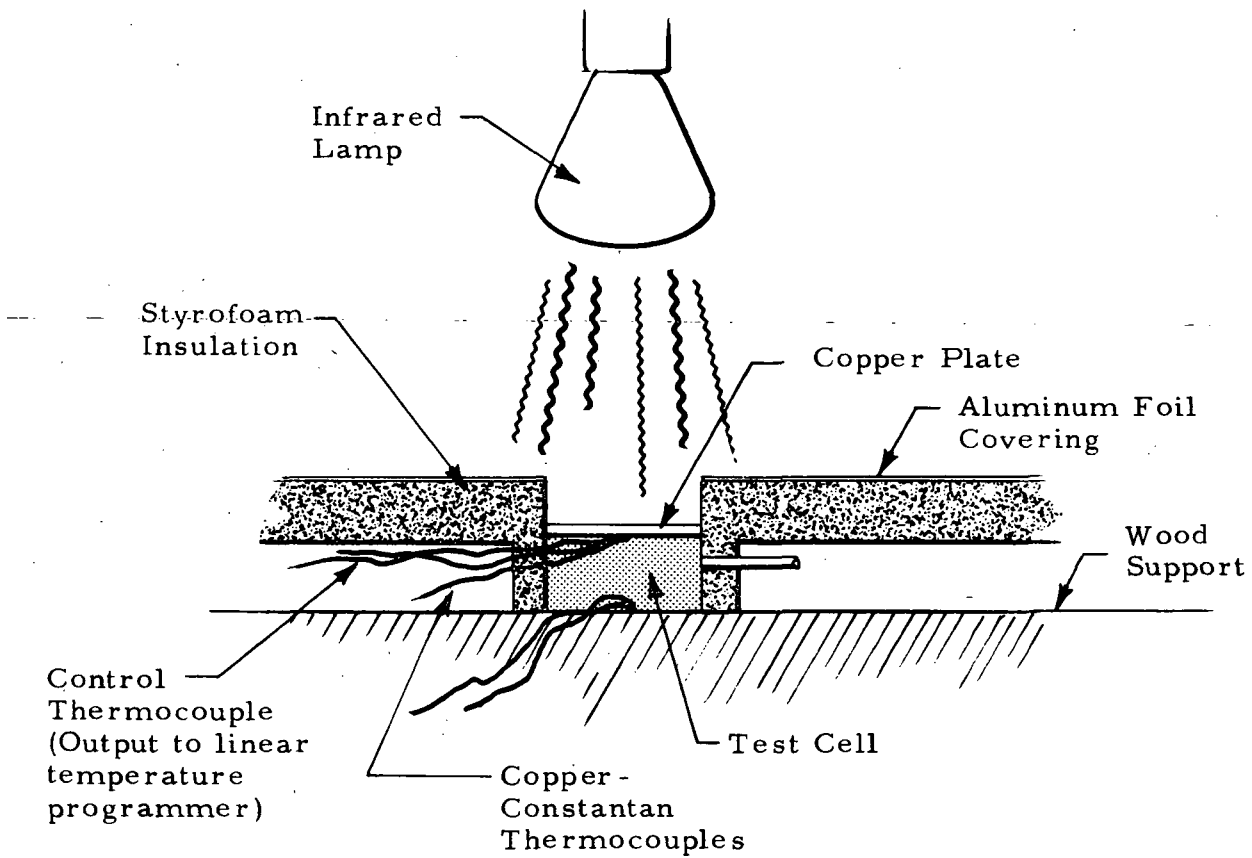
A-1

Infrared
Lamp

Styrofoam
Insulation

Copper Plate

Aluminum Foil
Covering

Wood
Support

Control
Thermocouple
(Output to linear
temperature
programmer)

Copper-
Constantan
Thermocouples

Test Cell

Fig. A-1 - Equipment for Measuring Thermal Diffusivity

Aluminum Foil

Plexiglas Cylinder
0.62 cm High

Tygon Tubing
Inlet for Filling
Cell with PCM

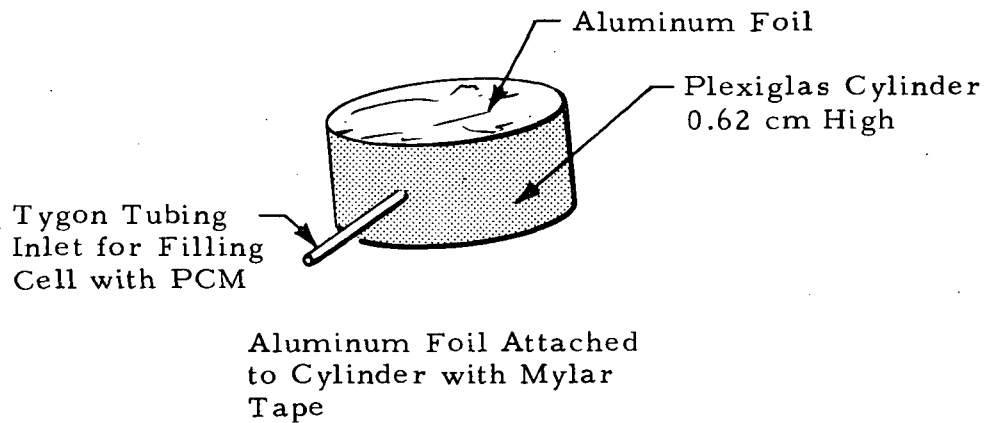Aluminum Foil Attached
to Cylinder with Mylar
Tape

Fig. A-2 - Detail of Test Cell Construction

A-2

A.2 EXPERIMENTAL OBSERVATIONS

The ideal condition of perfect thermal insulation is not practical, especially for materials having low thermal diffusivities. Such materials are so slow to respond to applied heat that considerable time is required for a temperature change to occur at the bottom of the cell. Most PCMs, with the exception of the metallic PCMs, are poor heat dissipators and have low values of thermal diffusivity. Therefore, most PCMs are slow to respond to applied heat, and the more time the test requires, the more heat leakage that can occur.

When several minutes of time are required for a temperature response to occur at the bottom (or far side) of the cell, the two parameters being measured deviate considerably from the ideal; that is, equal heating rates at the top and bottom of the cell are not attained and a constant temperature difference between the top and bottom of the cell is not achieved. Neither equal heating rates nor a constant temperature difference were obtained for the organic and inorganic PCMs tested; however, a solid disk of steel was tested for comparison with the nonmetallic PCMs. A quick response to heating, equal heating rates at the top and bottom of the disk, and a constant temperature difference between the top and bottom of the disk were obtained. The results calculated from Eq. (A.1) were in agreement with the reported value for steel. Steel and most other metals are able to equalize heat rapidly within themselves, so there is less chance of heat leakage to the surroundings than with nonmetals which are slow to equalize heat.

To illustrate the difference, Fig. A-3 depicts test data typical for steel and for a nonmetallic PCM. The graphs represent outputs from thermocouples at the heated top and unheated bottom of the test material. A constant temperature difference is obtainable with steel, and equal heating rates occur at the top and bottom of the steel disk. A quick response of the thermocouple at the bottom of the steel disk is clearly evident. On the other hand, a constant temperature difference and equal heating rates are not obtained with the
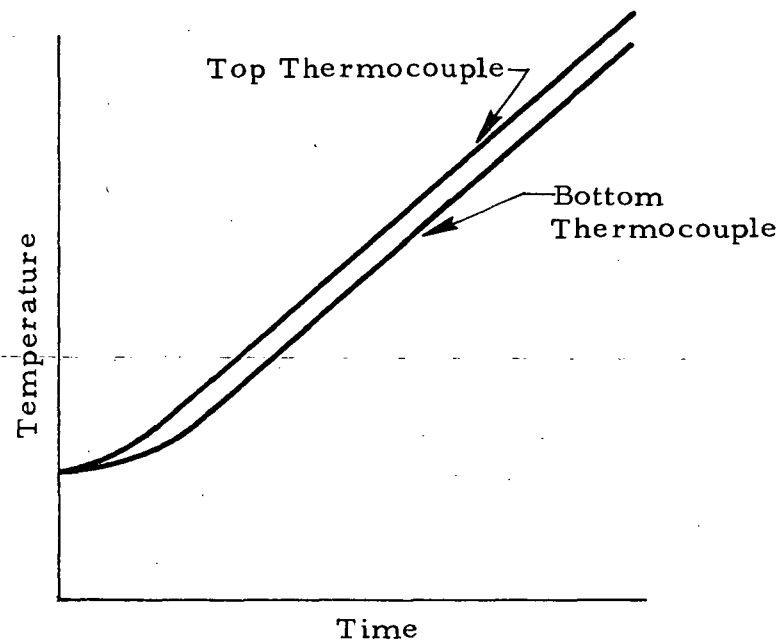
(a) Steel Disk
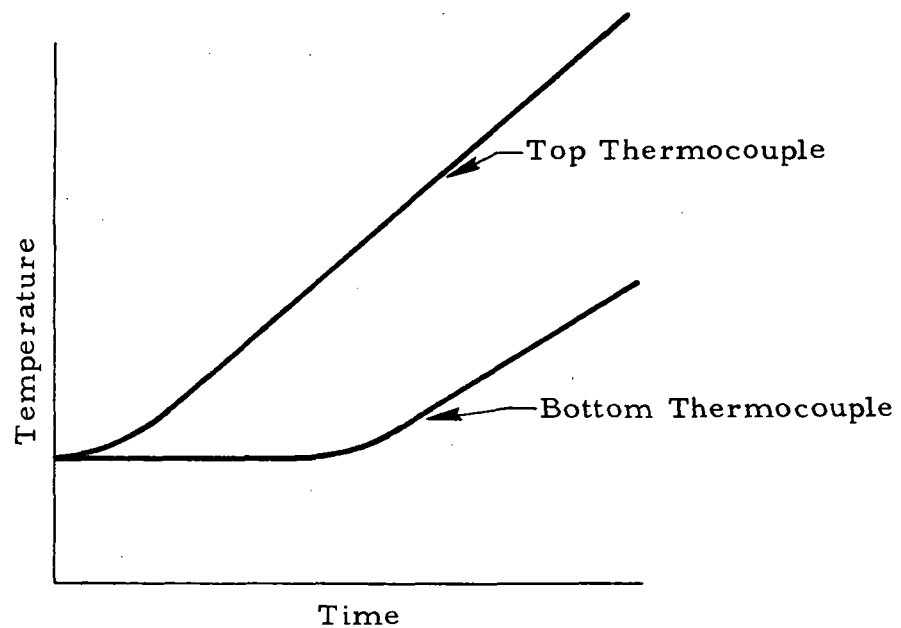
(b) Nonmetallic PCM

Fig. A-3 - Thermal Diffusivity Graphs for Steel and a Nonmetallic PCM

A-4

nonmetallic PCM. Furthermore, there is a considerable lapse of time between the time the heat is applied to the top of the test cell and a response as shown at the bottom of the test cell.

A.3 NEW METHOD FOR DATA TREATMENT

Most PCMs are nonmetallic and do not yield values of β and ΔT which satisfy the conditions of Eq. (A.1). Therefore a method was developed for interpreting the data obtained in tests. Data from a test run with water as the test material are given below. The term $f(\Delta T)$ represents the difference in scale readings at one minute intervals of the thermocouples at the top and bottom of the cell, which can be converted into millivolts and subsequently to degrees Kelvin. $\Delta f(\Delta T)$ represents the respective differences of $f(\Delta T)$.

f(ΔT)	Δf ΔT
5.8	-
12.7	6.9
19.4	6.7
25.0	5.6
29.8	4.8
33.8	4.0
37.2	3.4
40.4	2.2
43.1	2.7
45.5	2.4
48.0	2.5
49.9	1.9
51.7	1.8
53.3	1.6
54.5	1.2
55.7	1.2
57.0	1.2
58.1	1.2

When the value of $\Delta f(\Delta T)$ reached a final value of 1.2, it did not change, indicating that a quasi-steady state was reached. The value of $f(\Delta T)$ = 54.5 was taken to give a value for ΔT because $\Delta f(\Delta T)$ becomes constant at this point. (See Ref. 1 for a full discussion of this procedure.)

The value of β used was the heating rate of the top of the cell. The average thermal diffusivity of water using ΔT at the point where $\Delta f(\Delta T)$ becomes a constant and β as the heating rate at the top of the cell is 1.34×10^{-3} cm^2/sec (literature value of 1.35×10^{-3} cm^2/sec, Ref. page 2-3). With other materials, a precision of about 10% was achieved.

Although the graphs for the nonmetallic PCM may deviate greatly from the ideal, relatively precise and accurate results are obtainable with the indicated method for data interpretation. This method takes into account the possibility of a constant rate of heat leakage.

Appendix B

DIFFERENTIAL SCANNING
CALORIMETER THERMAL PROFILES

Appendix B

Methods of differential thermal analysis are based on the fact that thermal energy is absorbed or evolved during a physical or chemical change as a sample is heated or cooled. In the differential scanning calorimeter (DSC), the temperature can be programmed to either heat or cool a test sample and reference material at a choice of eight different heating or cooling rates. The sample and reference temperatures are continuously maintained at the same level. When the test sample absorbs or evolves energy, power is required, either more or less, to maintain the test sample at the same temperature of the reference holder. Since power is energy per unit time, the DSC records the rate of energy absorption as a function of test sample temperature. Consequently, a peak area represents the energy of the associated reaction.

The thermal profiles obtained with a DSC yield qualitative information on transitions such as melting, freezing, decomposition, glass transition, etc. Quantitative data in the form of heat of fusion or heat of melting are also given. The purity of the sample may also be determined. Any physical or chemical changes that occur in a PCM will be evident in the thermal profile. The thermal profile consists of peak areas corresponding to endotherms and exotherms. The shape and spacing of the peaks are repeatable if no changes have occurred in the PCM. When changes do occur such as a decomposition change in purity, or freezing point after long-term cycling, they are clearly evident because the thermal profile after cycling will not correspond to the thermal profile before cycling.

Appendix C

PREPARATION OF ZINC
HYDROXY NITRATE NUCLEATION CATALYST

Appendix C

A nucleating catalyst for PCM lithium nitrate trihydrate was previously discovered at Lockheed-Huntsville. This nucleating catalyst is zinc hydroxy nitrate ($Zn(OH)NO_3$). A sizable quantity of catalyst was prepared for further investigation under carefully controlled conditions. The product obtained nucleates lithium nitrate trihydrate and is believed to be a fairly pure sample of zinc hydroxy nitrate. The catalyst was prepared by the pyrolysis of zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) at a temperature of $473^{\circ}K$ for several hours. Properties of the resulting product are as follows:

- Thermal stability up to $364^{\circ}K$

- Decomposes without melting

- Endotherms[*] occur at three temperatures:

  $364^{\circ}K$ -   Possibly dehydrates at this temperature.

  $496^{\circ}K$ -   Color change takes place; a white solid changes into a yellow solid.

  $600^{\circ}K$ -   Copious quantities of nitrogen dioxide are discharged at this temperature.

Only two other specific nucleating catalysts are known, borax to nucleate Glauber's salt and iodides to precipitate rain from clouds. Isomorphous pairs with the same crystal structure like $NaH_2PO_4 \cdot 12H_2O$ and $NaH_2AsO_4 \cdot 12H_2O$ are limited to one-time nucleating agents for each other. Lithium nitrate trihydrate has an orthorhombic crystal structure, so possibly zinc hydroxy nitrate is also orthorhombic. A similar compound was found in the literature which is orthorhombic, zinc hydroxy chloride (Ref. 14). Although the field of nucleating catalysts is very limited, nucleating catalysts undoubtedly will be of prime importance in PCM technology.

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[*]Taken from a Differential Scanning Calorimeter (DSC) thermal profile.

Appendix D

CHEMICAL ASSOCIATION AND PCM
POTENTIAL

Appendix D

The behavior of PCMs in the solid state is more predictable and dependable than the behavior of liquid PCMs. Solid PCMs melt dependably at the melting point or over a melting range of a few degrees. Superheating a solid is almost never encountered. However, the reverse process of freezing a liquid PCM may present problems. Many liquids, especially associated liquids, supercool without freezing in the desired temperature range. Supercooling may amount to only a few degrees or over a hundred degrees as exhibited by glycerol. Therefore, a brief consideration of properties of liquids which are especially important in PCM technology are discussed in the following.

While there are many different types of liquids, they can be divided into two broad categories: normal and associated. Normal liquids are more uniform in behavior and thus easier to generalize about than associated liquids. Normal liquids approximately obey empirical relations concerned with properties such as crystallization, viscosity, boiling point, etc. Typical examples of normal liquids are argon, carbon tetrachloride, and most organic liquids (Ref. 12).

Associated liquids form double molecules or polymolecules as a result of moderately strong intermolecular forces. Associated liquids exhibit deviations from the empirical relations followed by normal liquids. One kind of widespread molecular association in PCMs is hydrogen bonding. Hydrogen bonding in water is responsible for its high heat of fusion and vaporization. Hydrogen bonding is displayed by phenols, alcohols, carboxylic acids (Ref. 8), and organic materials containing hydroxyl (OH) or amino (NH$_2$) groups (Ref. 12). The hydrogen atoms act as bridges to link the molecules together in molecules which have hydrogen atoms attached to small electronegative atoms, such as oxygen, nitrogen, or fluorine (Ref. 8). The

strength of hydrogen bond increases in the order F-H-F, O-H-O, O-H-N, N-H-N and C-H-O (Ref. 12). Some factors which affect the strength of hydrogen bonds are the geometry of the molecule, the nature of the near elements, and the acid and base characteristics of the hydrogen groups.

The properties of associated liquids depend upon the number of effective links the particles can form with each other. Water is a good example of a strongly associated liquid. Its heat of fusion is one of the highest of all PCMs. Generally, PCMs which are associated have high heats of fusion.

Although PCMs which form associated liquids have high heats of fusion, their behavior is more complicated than that of normal liquids. Supercooling is more common in associated liquids than in normal liquids. Normal liquids generally do not have high heats of fusion, so there are fewer normal PCMs than associated PCMs. However, since the behavior of normal PCMs is generally more predictable and dependable, their performance may be desirable for certain applications when all tradeoffs are considered.

Appendix E

EXPERIMENTAL CONCEPT FOR DETERMINATION OF VOLUME CHANGE UPON MELTING

Appendix E

The determination of volume change during melting by a Phase Change Material (PCM) can be found by two methods. The first method involves density measurements of both solid and liquid PCM near the melting/freezing point. The second method gives volume change on melting directly.

E.1 METHOD I

The density of liquid PCM near the freezing point can be found by weighing a sample and then measuring the volume of the sample with a graduated cylinder. The graduated cylinder can be placed in a constant temperature bath near the freezing point of the liquid PCM. The weight per unit volume gives the density of the liquid PCM.

The density of the solid PCM near the melting point can be found by weighing a sample and finding the volume occupied by that weight. The volume of solid PCM can be determined by the following procedure (Fig. E-1).

- Pour a quantity of an inert liquid into a graduated cylinder. Place the graduated cylinder in a constant temperature bath near the melting point of the PCM, and record the volume of inert liquid. Inert oils may be useful for water soluble materials. Water may be used with certain organic materials and metallics.

- Add a weighed sample of solid PCM to the inert liquid in the graduated cylinder. Surface active agents added to the inert liquid increase wetting ability. Record the volume of the inert liquid with solid PCM in it near the PCM melting point.

- The difference in the volume of the inert liquid with and without the solid PCM corresponds to the volume of solid PCM. The density of solid PCM can then be calculated.

Since the volumetric measurements are made in an essentially isothermal environment, the melting/freezing point of the PCM, volume changes in the inert liquid should be negligible.
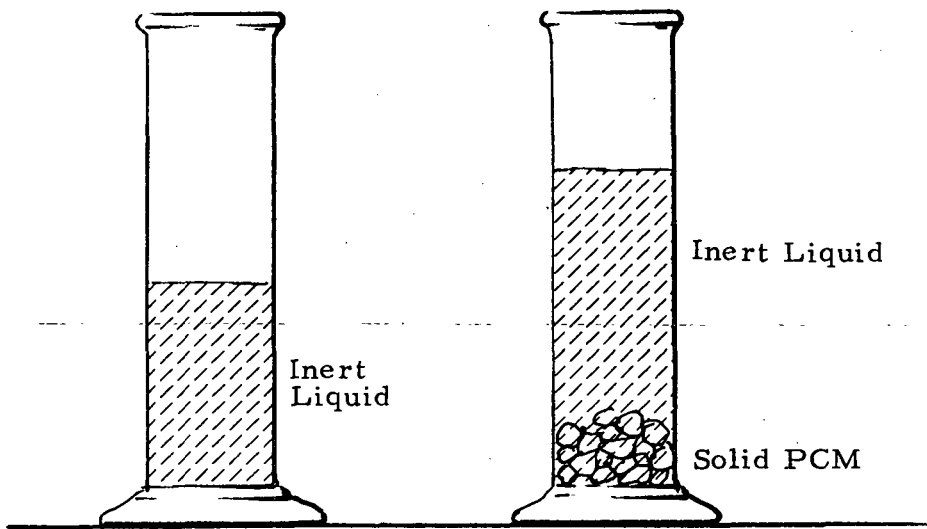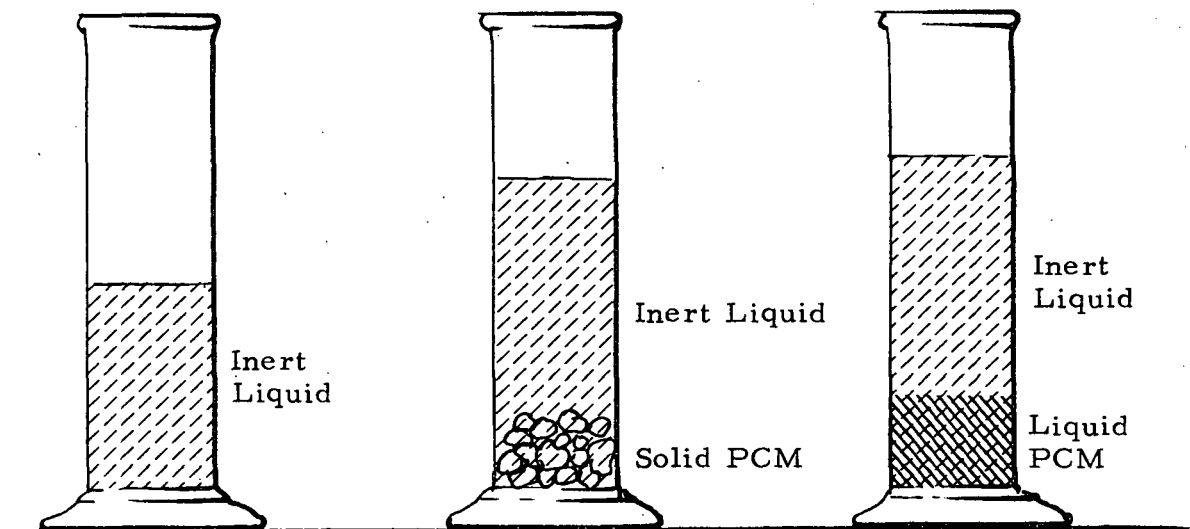
Fig. E-1 - Finding the Volume of Solid PCM

Fig. E-2 - Volume Change on Melting

E-2

E.2   METHOD II

A sample of solid PCM is added to a measured amount of inert liquid in a graduated cylinder (Fig. E-2).   The graduated cylinder with solid PCM and an inert liquid in it is then placed into a thermally controlled bath.   The temperature of the bath should be as near to the melting point of the PCM as possible without any PCM melting.   The volume of inert liquid with solid PCM is recorded.

The temperature of the bath is then raised to the PCM melting point. When the PCM is completely melted, the level of the inert liquid in the graduated cylinder is recorded.   The difference in the volume before and after melting corresponds to the volume change on melting.   Volumetric expansion of the inert liquid may be negligible since the temperature change is usually very small.   However, if the PCM melts over a range, the volume change of the inert liquid over that range should be measured.

If the volume change due to the inert liquid is significant, it should be taken into account and used in calculating the volume change due to PCM melting.